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EFFECT OF FUEL SULFUR ON NOx EMISSIONS FROM PREMIXED FLAMES

J. O. L. Wendt, et al

Arizona University
Tucson, Arizona

October 1975

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16. ABSTRACT The report gives results of an investigation of the effect of fuel sulfur compounds on nitrogen oxides (NOx) emissions from premixed gaseous flames. Laboratory measurements, using a methane/air flat flame doped with SO2 or H2S, showed that fuel sulfur inhibits the formation of NOx arising from thermal fixation. This inhibition was significant at all air/fuel ratios and especially at high air preheats. The effect of fuel sulfur on formation of NOx arising from fuel nitrogen oxidation is less clear because of complex reactions between sulfur- and nitrogen-containing species in both the flame and the sampling probe. A mathematical simulation of a flat flame was developed that showed that the observed effect of fuel sulfur on 'thermal NO' could be explained by a kinetic mechanism involving the catalysis of atom recombination reactions by SO2. The experimental and theoretical results may be especially significant from a practical point of view, since they appear to indicate that fuel desulfurization may lead to increased NOx emissions.

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by

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PURPOSE AND SCOPE

The objective of this work was to determine the conditions under which fuel sulfur inhibits the formation of nitrogen oxides in flames. The importance of this project lies in the need to determine whether fuel desulfurization might have an adverse effect on nitrogen oxide emissions.

The study consisted of three phases. In Phase I we examined through controlled laboratory experiments, the effect of fuel sulfur on nitrogen oxide formation by atmospheric fixation (Thermal NO). In these experiments fuel sulfur was simulated by addition of sulfur dioxide and hydrogen sulfide to a nitrogen free gaseous fuel which was then mixed with air to burn in a premixed laminar flat flame. The ensuing interactions between sulfur and thermal NO formation mechanisms were then examined in some detail, and conclusive results were obtained. In Phase II, we examined, using the same apparatus, the effect of fuel sulfur on nitrogen oxide formation by fuel nitrogen conversion (Fuel NO). Fuel nitrogen compounds were simulated by addition of NO itself and of cyanogen, C_2N_2. Results of this phase were not conclusive, and should be regarded as preliminary. In a contiguous Phase III effort we focused our attention of sulfur dioxide-thermal NO interactions and developed a mathematical model that describes quantitatively the effects measured experimentally in Phase I. The model involves a computer simulation of a flat flame and is described in detail. The model was developed so that observed effects could be interpreted and explained in the light of fundamental principles. The computer code developed was supplied to EPA.

CONCLUSIONS

It was found that both sulfur dioxide and hydrogen sulfide, when added to a gaseous fuel, had a significant inhibition effect on thermal NO_x emissions. The presence of sulfur to make about 6800 ppm SO_2 in the exhaust lowered NO_x emissions by up to 36%. Although it should be noted that these results are valid for premixed gaseous flames, they do imply that fuel desulfurization may lead to increased (thermal) NO_x emissions from combustion processes.

It appears to make very little difference whether the fuel sulfur is introduced into the fuel as SO_2 or H_2S, except under fuel rich conditions where conversion of H_2S to SO_2 is not rapid. This indicates that the inhibition of NO formation by fuel sulfur occurs through mechanisms involving SO_2.

The data on the effect of fuel sulfur on fuel NO emissions are inconclusive, due to previously unreported phenomena occurring in quartz sampling probes under fuel rich conditions. However, preliminary indications are that although the effect of fuel sulfur on fuel NO emissions is not significant under fuel lean conditions, it may under fuel rich conditions have a marked influence on the rate at which fuel NO is formed.

A preliminary analytical model of a premixed flat flame showed that the inhibition effect of fuel sulfur on "Thermal NO" could be explained by the homogeneous catalysis of free radical recombination rates by sulfur dioxide. This mechanism lowers the oxygen atom concentration, when this concentration is above the

equilibrium value, and, for a given radiative heat loss, lowers NO formation rates. The effect of lower oxygen atom concentrations is greater than the ensuing (coupled) temperature increase. Under conditions where the temperature was fixed as an independent variable the theoretically predicted inhibitory effect of SO_2 on thermal NOx emissions was even larger. Observations involving inhibition of NO formation by SO_2 might therefore be used to arrive at conclusions concerning the role of superequilibrium oxygen atoms. This is true even when the primary NO formation mechanism does not involve oxygen atoms directly, since the concentrations of other important atoms and free radicals are intimately related and coupled to that of the oxygen atom. Since inhibition was observed under fuel rich and fuel lean conditions it appears that superequilibrium oxygen atoms and other free radicals play an important role in both regimes. The effect of SO_2 was especially pronounced on "prompt" NO formation, and this supports theories that superequilibrium concentrations of oxygen atoms and other radicals are a factor in the rapid formation of NO early in the flame. In addition, the experimental results on the thermal NO showed that "prompt" NO accounted for essentially all the NOx emission under fuel rich conditions and that it was not a strong function of mixture preheat. This implies that NOx formation mechanisms other than those of Zeldovich are controlling early in the flame.

RECOMMENDATIONS

Future work should concentrate on three areas in order to identify the practical aspects of the results of the research reported here. First, the effect of fuel sulfur on NO_x emissions from oil and coal diffusion flames should be investigated, in order to determine if fuel desulfurization in general will have an adverse effect on NO_x emissions from combustion units of practical interest. Second, the more fundamental aspects of fuel sulfur and fuel nitrogen interactions during the combustion process should be examined further, since an understanding of these phenomena will aid in the interpretation of new data, and in the identification of future potential environmental problems associated with fuel desulfurization. Third, theoretical tools should be developed in order to allow effects observed from laboratory scale premixed flame experiments to be extrapolated with some confidence to oil and coal diffusion flames in practical combustion units. Laboratory experiments, such as are reported here are relatively fast and inexpensive, and it would be useful to be able to deduce the correct practical implications of observed phenomena without having to resort to expensive and difficult full scale tests.

BACKGROUND

The combustion of many fossil fuels gives rise to emissions of both sulfur oxides and nitrogen oxides. Sulfur oxide pollution may be abated by either fuel desulfurization or stack gas scrubbing. The choice of abatement method is usually dictated by economic considerations. However, in calculating the cost effectiveness of various sulfur oxide abatement strategies it is important to determine the extent to which the technology used has an adverse effect on other pollutants, such as NO_x. Should sulfur compounds in the flame front have an inhibition influence on the formation of NO_x this would indicate that fuel desulfurization might require additional NO_x abatement methods to be implemented, and that this would involve additional costs which would not occur with stack gas scrubbing where the sulfur species are removed after the combustion process.

That sulfur and nitrogen oxides interact at low temperatures is not new[1,2]. This interaction results in the catalysis, by NO, of the oxidation of SO_2 to SO_3. At higher temperatures, under combustion conditions, the situation is quite different and a clear distinction should be drawn between low temperature and high temperature interactions. At high temperatures under combustion conditions, free radicals are produced in superequilibrium amounts and this fact has been shown to be important in explaining high NO production rates[3,4] where the NO is formed by atmospheric fixation (Thermal NO). Since it has been shown[5,6] that sulfur dioxide is an effective catalyst in reducing superequilibrium free radical concentrations, it is reasonable to expect that sulfur dioxide and possibly other fuel

sulfur compounds, inhibit the formation of NO in flames. In order to explore this possibility further, it is necessary to focus on certain fundamental aspects of NO formation mechanisms. In spite of much research in this area, there is even now no general agreement on the kinetic mechanisms of thermal NO production. Most widely recognized as being important is the mechanism proposed by Zeldovich[7]:

$$N_2 + O \rightarrow NO + N \quad (1)$$

$$N + O_2 \rightarrow NO + O \quad (2)$$

with the modification

$$N + OH \rightarrow NO + H \quad (3)$$

and with the free radicals necessary for these reactions being produced through the combustion process. It should be noted that the free radicals so produced can have concentrations many fold in excess of those determined by equilibrium and that the decay of these radicals towards equilibrium is relatively slow and occurs downstream from the flame front. Under fuel lean conditions, it is in this region of free radical decay that a substantial portion of the NO is formed through reactions (1) through (3). Thompson and Beer[3] have shown that indeed, superequilibrium concentrations of oxygen atoms are responsible for high rates of NO formed in their apparatus and their conclusion was corroborated by other workers,[4,8] especially as regards NO formation in the fuel lean regime. In the fuel rich regime, however, it appears that for hydrocarbon flames, an NO formation mechanism involving cyanide compounds as intermediates may be applicable[4,9], and under these conditions the role of superequilibrium atom and radical concentrations is unclear. It is generally recognized, however, that high rates of NO formation can result from superequilibrium atom concentrations, and it would therefore appear that catalysts and other impurities,

such as SO_2, that have been shown to decrease radical concentrations, should tend to lower thermal NO formation rates.

In order to determine the effect of fuel sulfur on thermal NO it is necessary to devise a well defined laboratory experiment to answer the following questions:

- Does SO_2 have an inhibitory effect on thermal NO emissions?
- Under which conditions is any inhibtion of NO formation by SO_2 most significant?
- Does SO_2 affect the formation of "prompt NO" and if so what conclusions can be drawn about the role of superequilibrium atom concentrations and "prompt NO"?
- With H_2S in the fuel, is conversion of the fuel sulfur to SO_2 sufficiently rapid to allow the SO_2 formed to have the same effect as when added directly to the fuel?

Literature on flame interactions between species derived from fuel sulfur and fuel nitrogen in the flame front is quite meager. Yet the problem of fuel sulfur effects on fuel NO emissions is of substantial practical interest since most fuels that contain fuel sulfur contain appreciable amounts of chemically bound nitrogen. Desulfurization of a fuel does not necessarily lead to a proportional decrease in the fuel nitrogen content.

Since the mechanisms of fuel nitrogen oxidation are presently quite imperfectly understood, and since the role of superequilibrium oxygen atoms in these mechanisms is unclear, speculation on the effect of fuel sulfur is at this point somewhat premature. Preliminary experimental results are first required to help orient our thinking on this question. However, recent work of Flagan *et al.*[10] indicates that superequilibrium concentrations of atoms and free radicals may play a role and this might lead us

tentatively to speculate that sulfur dioxide may have an inhibitory effect similar to that hypothesized for thermal NO. Moreover, according to Flagan *et al.*[10] it makes little difference in what form fuel nitrogen is introduced and so even NO itself could be considered a fuel nitrogen compound. It is therefore instructive to simulate fuel nitrogen by both NO and by an equivalent amount of cyanogen (C_2N_2). Although ammonia has often been used as a representative fuel nitrogen compound[8,10], it is not suitable for this study since it reacts with both SO_2 and H_2S to form solid sulfite and bisulfite salts before combustion is initiated.

In order for laboratory results to be extrapolated to other conditions, it is also necessary to develop theoretical mathematical models that describe the appropriate kinetic mechanisms, and that can be used to determine the significance of the results in other, more practical combustion environments. In particular, mathematical models will give insight into fundamental questions such as

- Can the observed effect be explained by catalysis of atom and radical recombination rates by SO_2?
- What can be expected under different time temperature histories?
- What can be expected in real furnace flames?

EXPERIMENTAL APPARATUS

COMBUSTION RIG

A schematic of the premixed combustion rig and supporting equipment used is shown in Figure 1 and a diagram of the burner itself in Figure 2. Meted amounts of methane (Matheson, C.P.), preheated house air, and when applicable, SO_2 or H_2S (Matheson, C.P.), were allowed to mix, then preheated further before being fed into a modified Meker burner. The temperature of the gas mixture entering the burner was controlled. The Meker burner was modified so that an approximately flat flame could be supported above the burner grid. The burner was at atmospheric pressure and enclosed in a pyrex glass chimney.

The combustion rig was designed primarily for a large number of input/output measurements rather than for detailed in-flame probing. However, some detailed probing was successfully attempted, and this showed that the flame could be considered flat to within our experimental error.

Incomplete temperature profiles taken with an uncoated 0.001" Pt-Pt/10% Rh thermocouple showed that the flame had temperatures in excess of 2000°K, even with no air preheat. This means that heat loss to the surroundings was not great, and might distinguish this flat flame from others[11,12].

SAMPLING AND ANALYSIS TRAIN

A schematic of the sampling and analysis train is shown in Figure 3. The sample was drawn through a 1mm diameter orifice into a 6mm OD, uncooled, quartz sampling tube. Preliminary

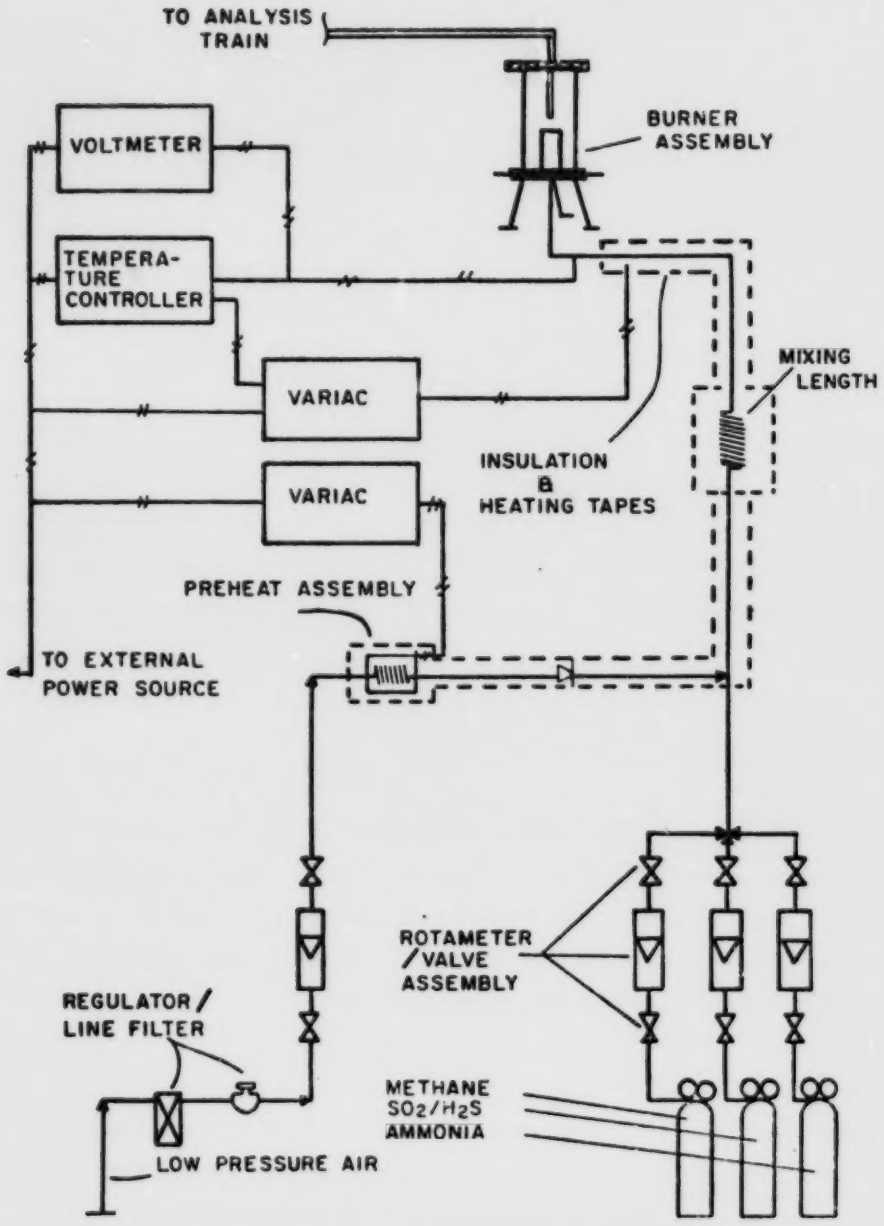

FIGURE 1. SCHEMATIC OF APPARATUS

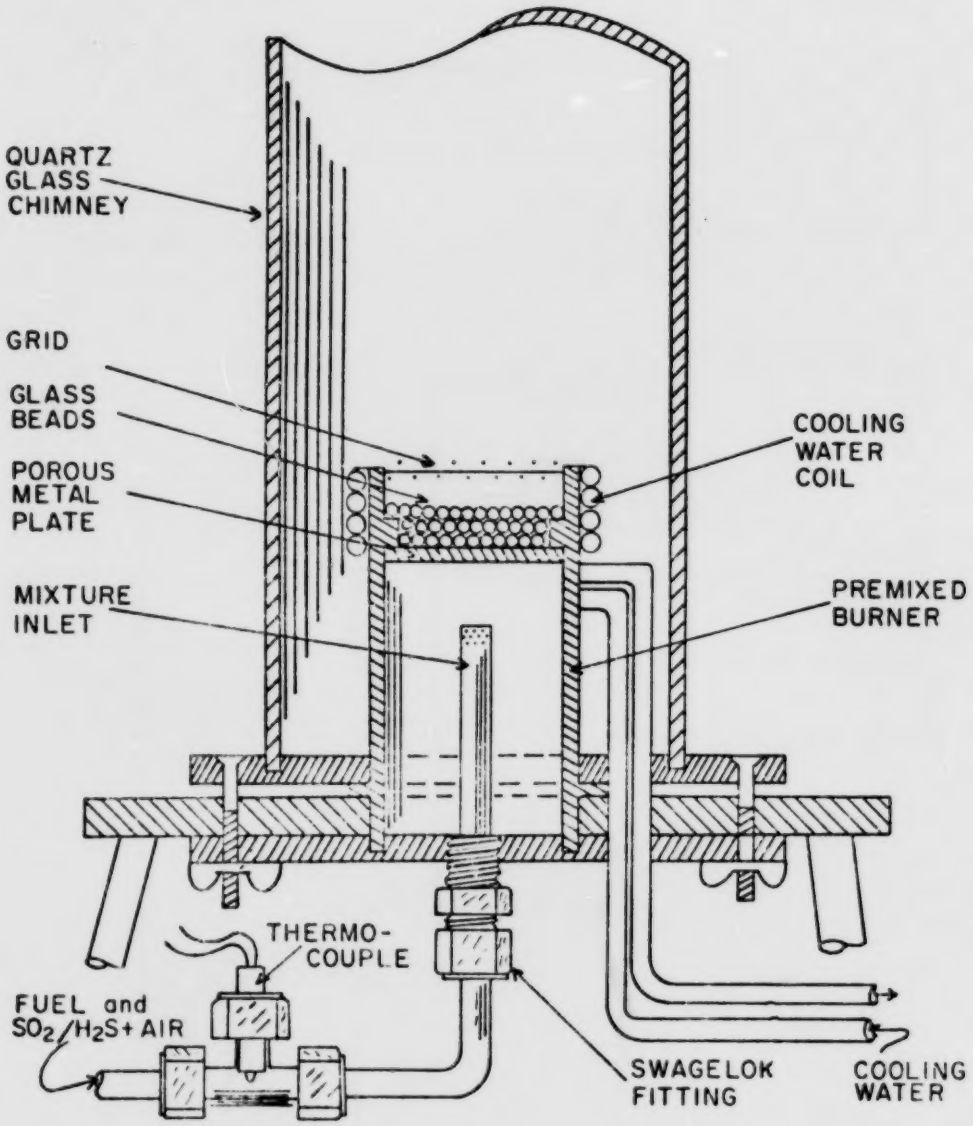

FIGURE 2. FLAT FLAME COMBUSTOR

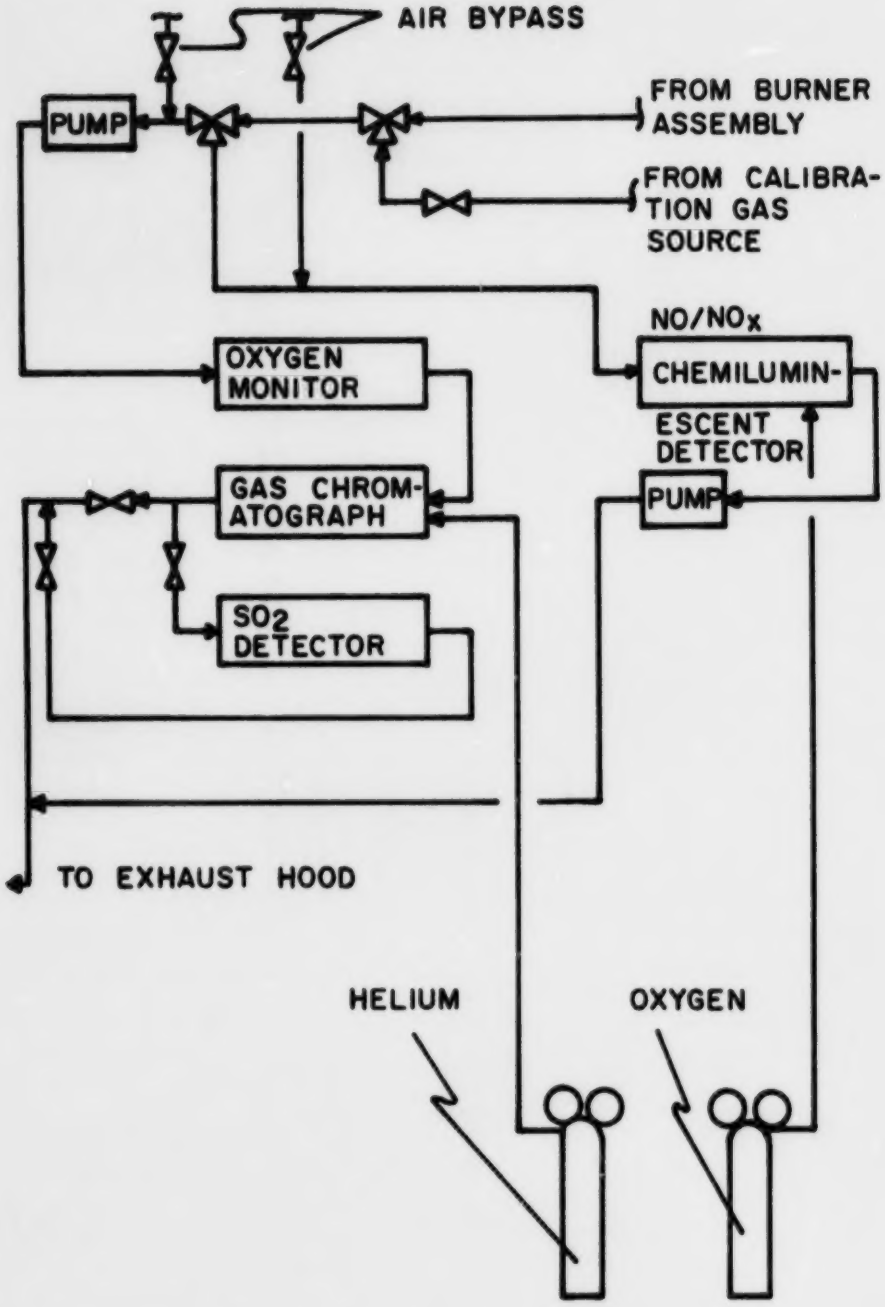

FIGURE 3. SCHEMATIC OF ANALYSIS SYSTEM

experiments in which the sampling rate was varied by a factor of four showed that our data did not depend on sampling rate and this, together with data from other experimentalists[13] indicates that all reactions were effectively rapidly quenched and no further reaction took place in the tube. The height of the sampling tube could be positioned accurately to within 0.03 mm.

Quartz and teflon tubing were used throughout the sampling and analysis train since stainless steel tubing has been shown to interfere with NO analysis under rich conditions. A cooled knockout pot removed moisture in the burned gas sample. The analysis train had the following features:

- NO/NO_x analysis by Thermo Electron Chemiluminescence Analyzer with stainless steel convertor
- O_2 analysis by Beckman Model 715 (Electrochemical) O_2 Monitor
- CO analysis by chromatograph with Porapak Q column
- SO_2 analysis by Theta Sensors SO_2 (Electrochemical) Monitor

The chemiluminescence analyzer worked perfectly and showed no interference by SO_2, O_2 or CO. This confirmed previous results[14] which showed that SO_2 does not interfere with (Thermo Electron) chemiluminescence measurements of NO.

For the Phase II results, the analysis train had the following additional features

- Molybdenum converter for Thermo Electron NO/NO_x analyzer
- CO analysis by NDIR, Beckman Instruments
- SO_2 analysis by Thermo Electron Pulsed Fluorescent SO_2 Analyzer

RESULTS

PREMIXED COMBUSTOR PERFORMANCE

Figure 4 and Figure 5 show results obtained with no SO_2 or H_2S added to the fuel. These are the base cases showing exhaust NO emissions as functions of air fuel ratio, air preheat (Figure 4) and NO concentration within the flame as a function of residence time from the burner (Figure 5). Figure 4 shows that with no preheat a maximum of 152 ppm (dry, reduced to 100% stoichiometric air NO was obtained at 104% stoichiometric air while with 240°C air preheat the maximum was 232 ppm. There is also a strong dependence on air fuel ratio. Figure 5 shows that formation of NO was complete at 6 cm above the burner grid or after a residence time of approximately 20 milliseconds and that sampling at that point was truly representative of exhaust NO emissions. Figure 5 also shows that under fuel rich conditions all the NO is formed very early in the flame and that this "prompt NO" was not a strong function of air preheat and that more "prompt NO" was formed under fuel rich conditions than under fuel lean conditions. These results agree qualitatively with those of Fenimore[9].

The ppm NO measured, under no preheat conditions, is substantially greater than that measured by other workers in flat flames[12]. This is probably due to the low heat loss rate in our system, and by the resulting high temperatures. The existence of temperatures well above 2000°K was confirmed by (incomplete) temperature measurements[15].

At each point (Figure 5) under fuel lean conditions both NO and

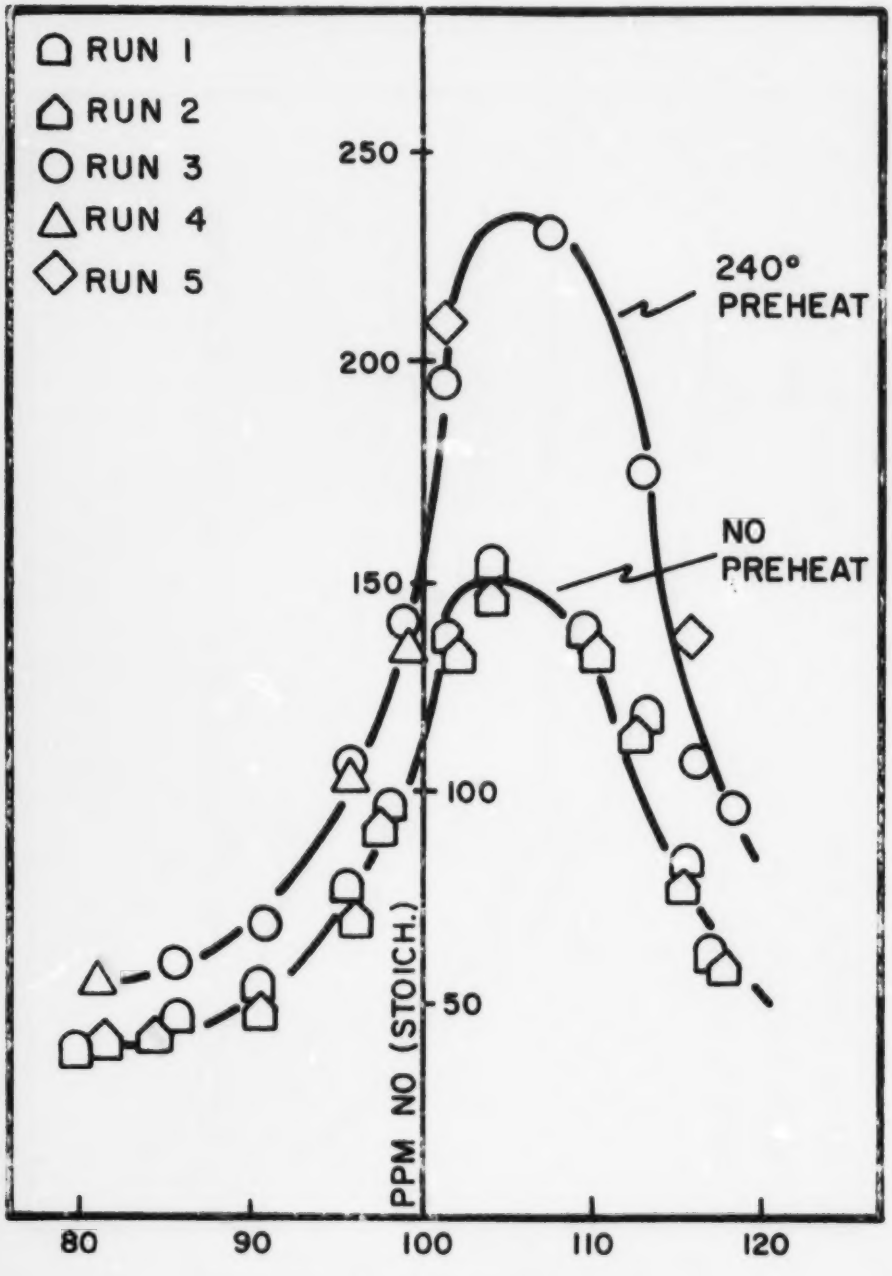

FIGURE 4. THERMAL NO EXHAUST EMISSIONS - BASE CASE

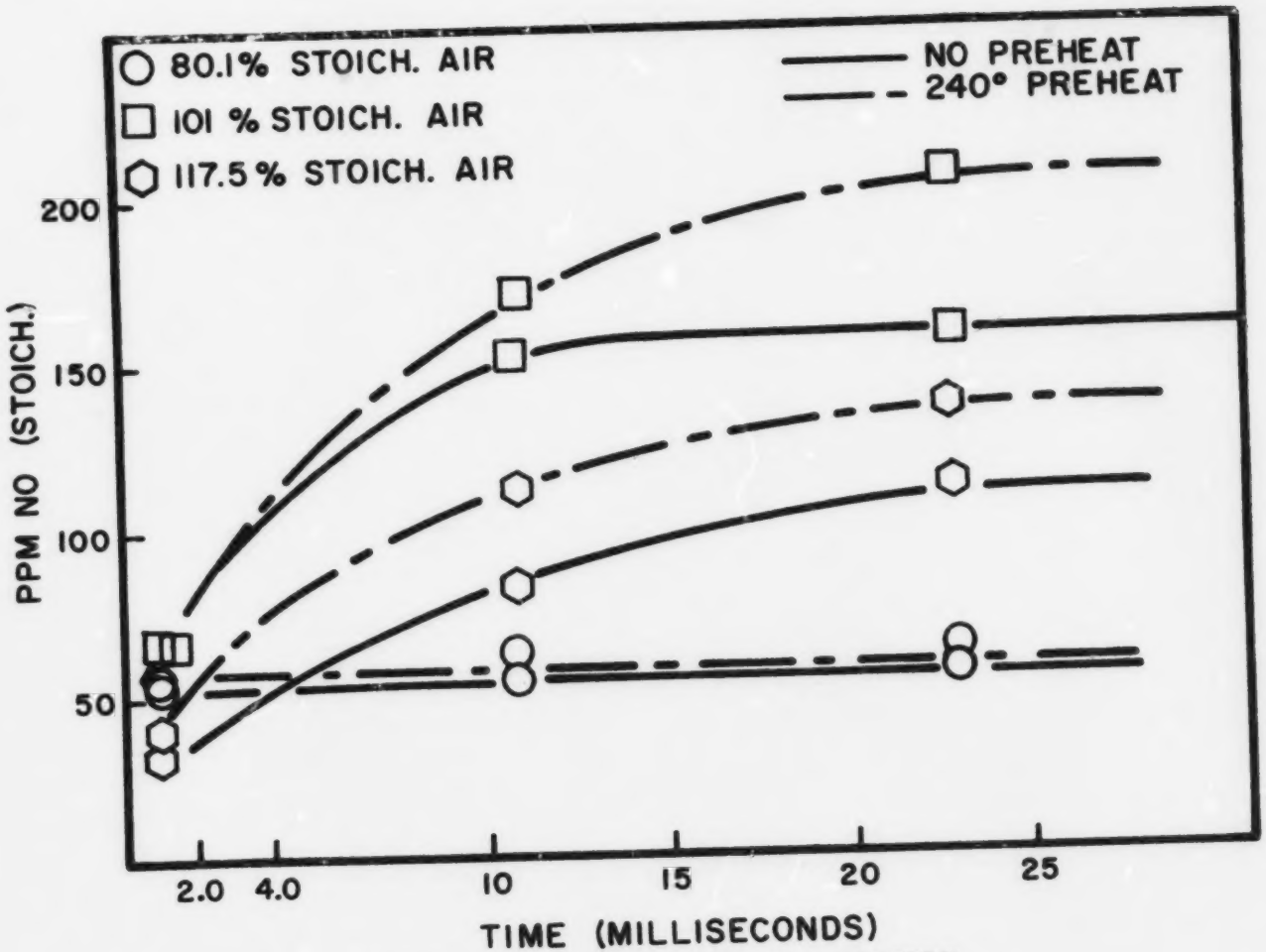

FIGURE 5. EXHAUST LEVELS OF NO ACHIEVED RAPIDLY

NO_x were measured by the chemiluminescent analyzer. At most 3 ppm NO_2 were observed, and then only under very fuel lean conditions. We thus did not observe any appreciable early NO_2 formation as reported by Merryman and Levy[16].

Additional runs were also made to investigate whether the addition of a fuel additive, such as SO_2, would lower NO emissions significantly by virtue of dilution alone. With molecular N_2 as the fuel diluent at zero preheat, 104% stoichiometric air, it was found that 10% N_2 in the fuel led to a reduction of less than 7 ppm NO in the exhaust. This means that any effect (larger than this) due to addition of up to 5% SO_2 to the fuel is due to kinetic interactions and not just simple dilution and temperature reduction.

PHASE I. EFFECT OF SO_2 ON THERMAL NO_x EMISSIONS

The effect of SO_2 as an additive in the fuel on the exhaust emissions of nitrogen oxide is shown in Figures 6 and 7. In Figure 6 the ppm NO (dry, reduced to stoichiometric) in the exhaust is shown in the absence of air preheat with and without 4.9 percent by volume SO_2 <u>in the fuel</u>. 4.9 percent by volume SO_2 in methane leads to approximately 6800 SO_2 in the exhaust. This sulfur level is considerably higher than that resulting from typical fossil fuels, and corresponds roughly to that for coal containing eight percent sulfur by weight. It can be seen that at approximately 101% stoichiometric air, 4.9% SO_2 in the fuel lowers NO exhaust emissions by 50 ppm or by about 36%. At other air/fuel ratios the percent reduction is somewhat less as shown on Table 1. At a preheat of 240°C (Figure 7) and at 101.% stoichiometric air the addition of 4.9% of SO_2 in the fuel lowers NO_x emissions by about 60 ppm or 30%. Conversely, looking at the effect of removal of SO_2 from the fuel one can say in this case, fuel desulfurization caused increases in thermal NO_x emissions of up to 55%.

Further details are shown in Table 1 in which results from two

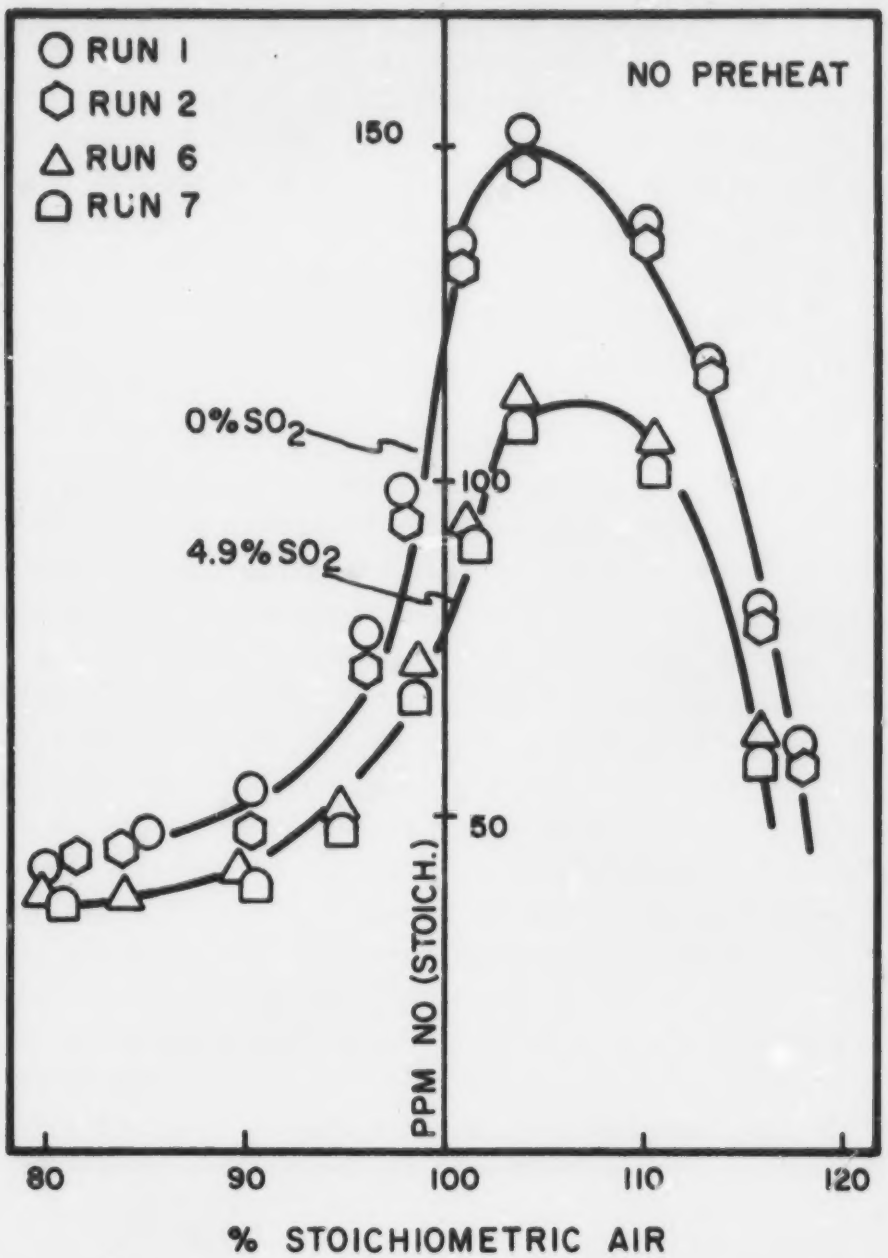

FIGURE 6. SO_2 INHIBITS NO FORMATION AT ZERO PREHEAT

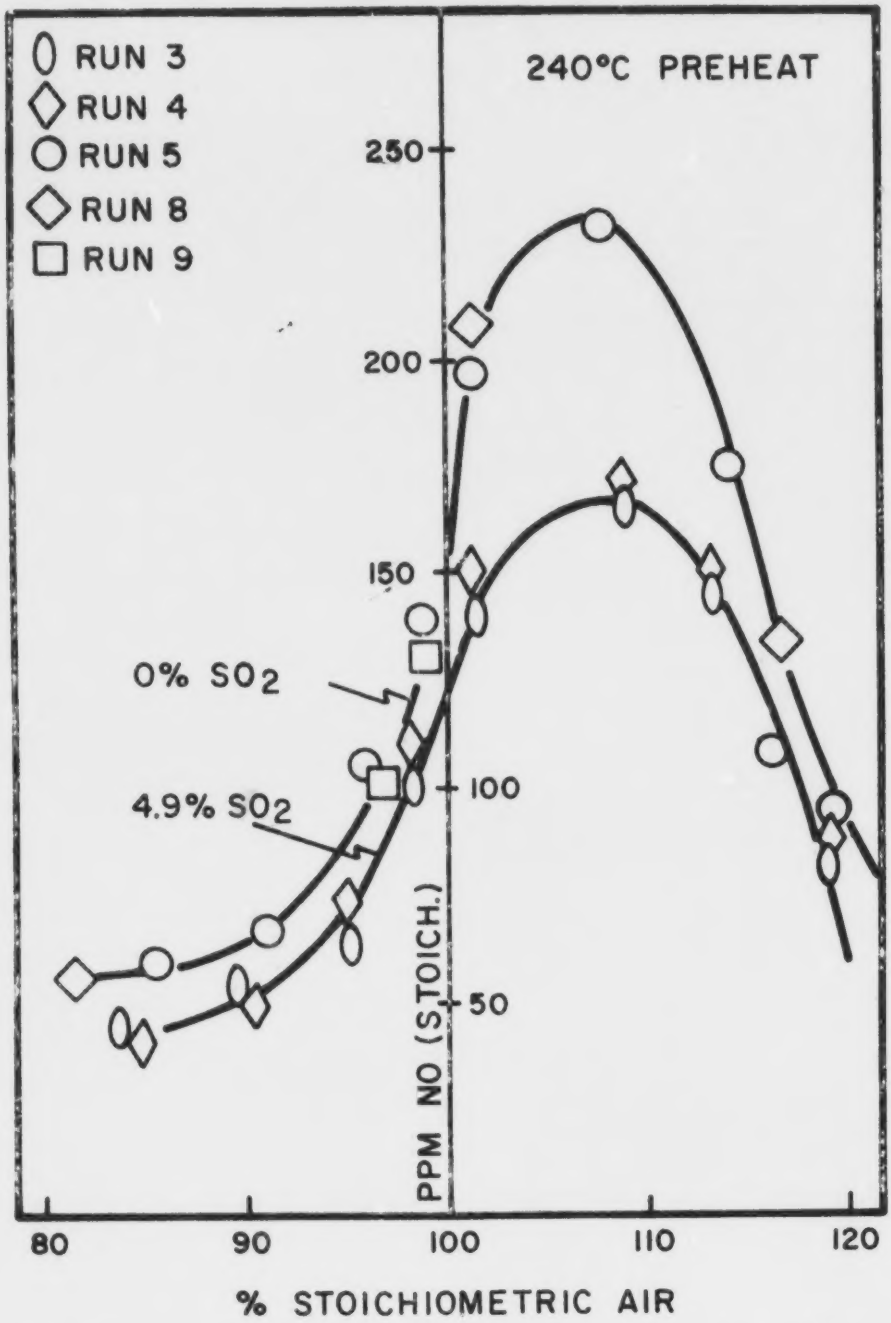

FIGURE 7. SO_2 INHIBITS NO FORMATION AT HIGH PREHEAT

Table 1. REDUCTION IN THERMAL NO_x EMISSIONS BY SO_2 ADDITION TO FUEL

Percent Stoichiometric Air	Reduction in NO_x Emissions							
	2.5% SO_2 in Fuel				4.9% SO_2 in Fuel			
	no preheat		240°C preheat		no preheat		240°C preheat	
	ppm	%	ppm	%	ppm	%	ppm	%
80.1	7	12.6	6.0	10.7	6.0	16.0	13.0	24.6
90.0	--	--	--	--	9.0	17.3	15.0	23.1
101.3	22.0	14.0	21.0	10.7	50.0	35.7	60.0	30.9
103.0	--	--	--	--	40.0	26.0	68.0	30.4
110.0	--	--	--	--	27.0	24.5	60.0	26.4
117.4	12.0	11.7	37.0	27.4	16.0	13.9	22.0	21.6

different flames are presented. (Flame 1 has slightly lower base case NO emissions). These results clearly show that as the SO_2 level in the fuel decreases so does reduction in NO_x emissions. With less than 1% SO_2 in the fuel any inhibition effect was not significant.

Figure 8 shows the results of probing within the flame (118.5% stoichiometric air, 4.9% SO_2 in the Fuel) and clearly demonstrates that at both preheats the effect of SO_2 is to quench the formation of NO fairly early in the flame. This data give insight into a probable kinetic mechanism as described later.

In Figure 9 the effect of 2.5% and 4.9% SO_2 on the formation of "prompt NO" is shown, where "prompt NO" is defined in this case as that formed within 0.3 cm of the burner grid. It should be noted that our definition of "prompt NO" differs from that of Fenimore, in that he defined it as the intercept of a linear extrapolation of the NO concentration profile back to zero residence time. It can be seen that at both preheats and at all air fuel ratios, the effect of increasing SO_2 is to decrease "prompt NO" formation. This indicates that superequilibrium concentrations of atoms and free radicals might be important under all air/fuel ratio conditions.

PHASE I. EFFECT OF H_2S ON THERMAL NO_x EMISSIONS

In Fossil fuels, sulfur is normally present in the reduced state. Thus, some experiments were completed with H_2S as the fuel additive, in order to determine whether fuel sulfur in this form has an effect on thermal NO_x formation.

Figures 10 and 11 show the effect of H_2S addition at two levels of mixture preheat. Since H_2S is a fuel, addition of this compound changes the air fuel ratio, and this has been taken into account in labeling the abscissa axis. In Figure 10 it is clear that both 2.6% and 5.0% H_2S in the fuel, with no mixture preheat, inhibit the formation of NO_x. NO_x emissions were reduced

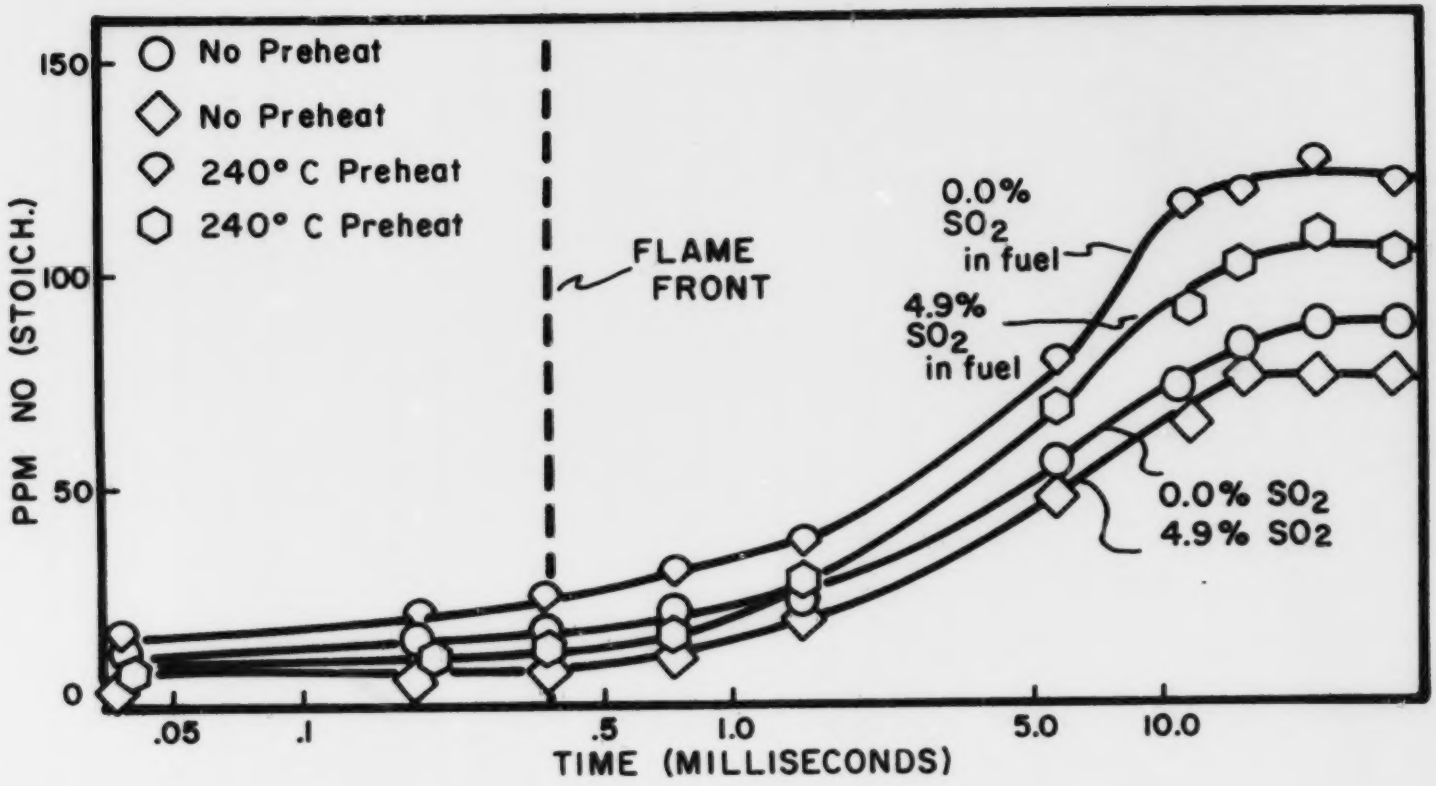

FIGURE 8. SO_2 DECREASES RATE OF NO FORMATION NEAR THE FLAME

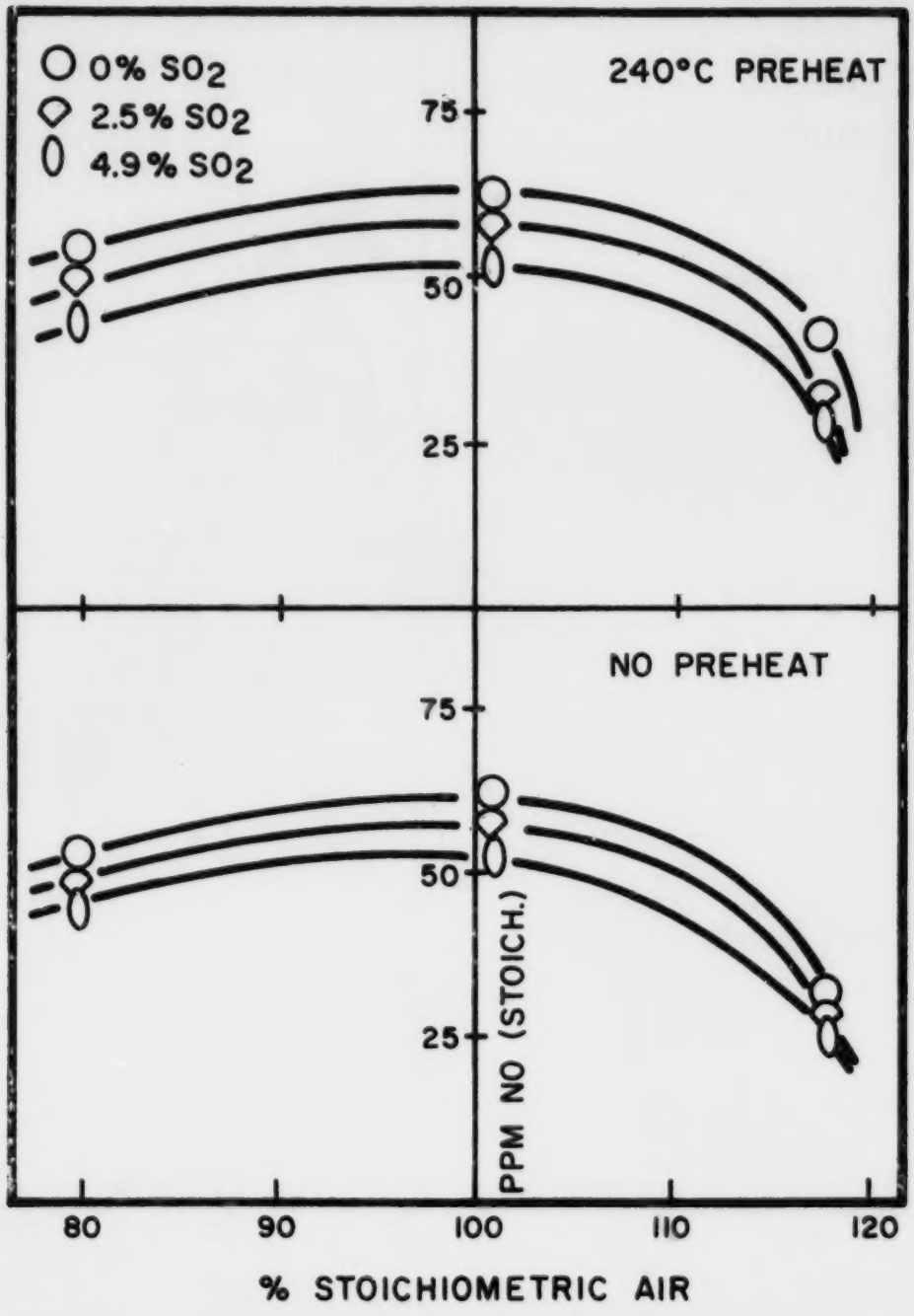

FIGURE 9. EARLY-FORMED NO INHIBITED BY SO_2

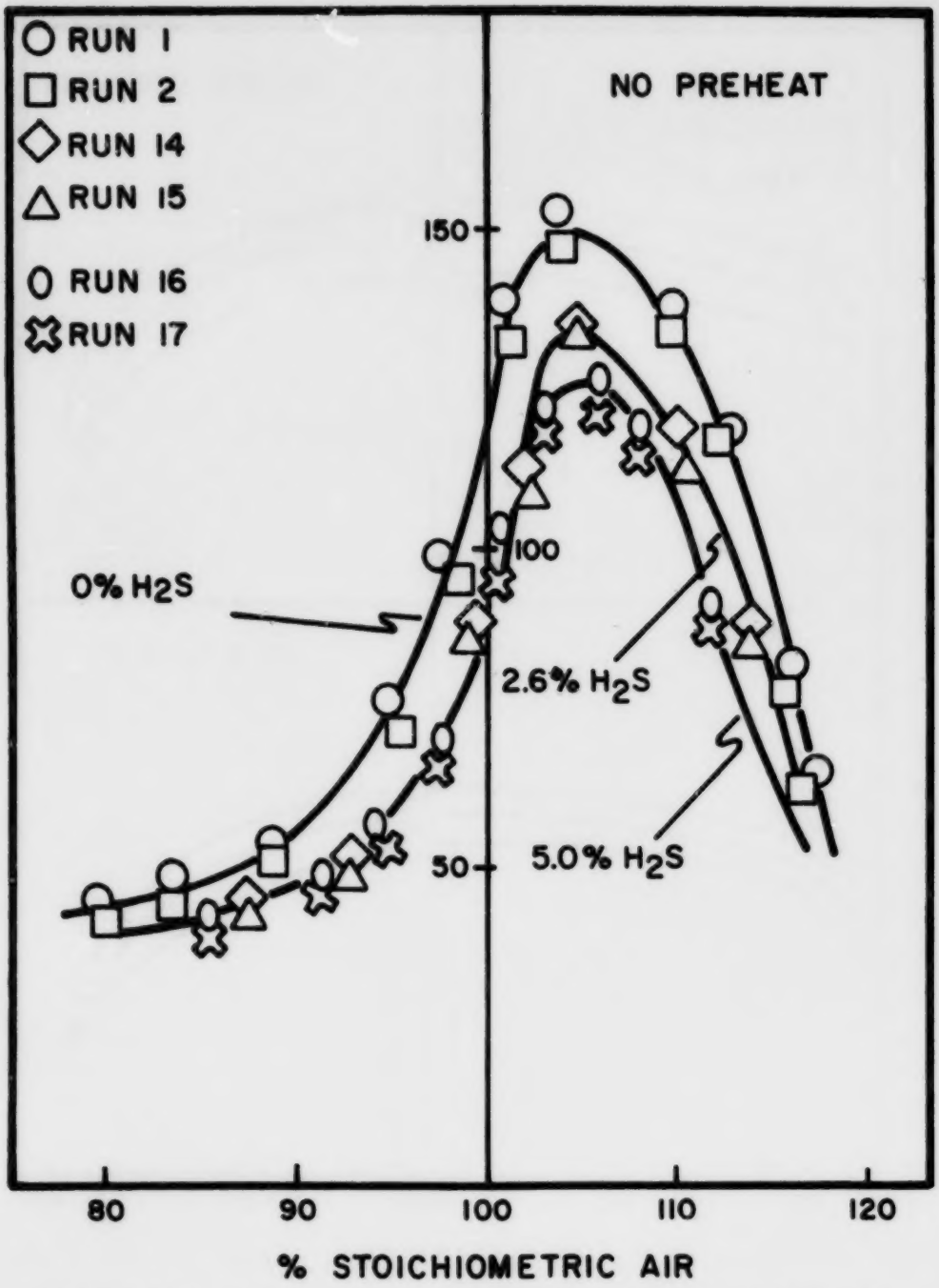

FIGURE 10. H_2S INHIBITS NO FORMATION AT ZERO PREHEAT

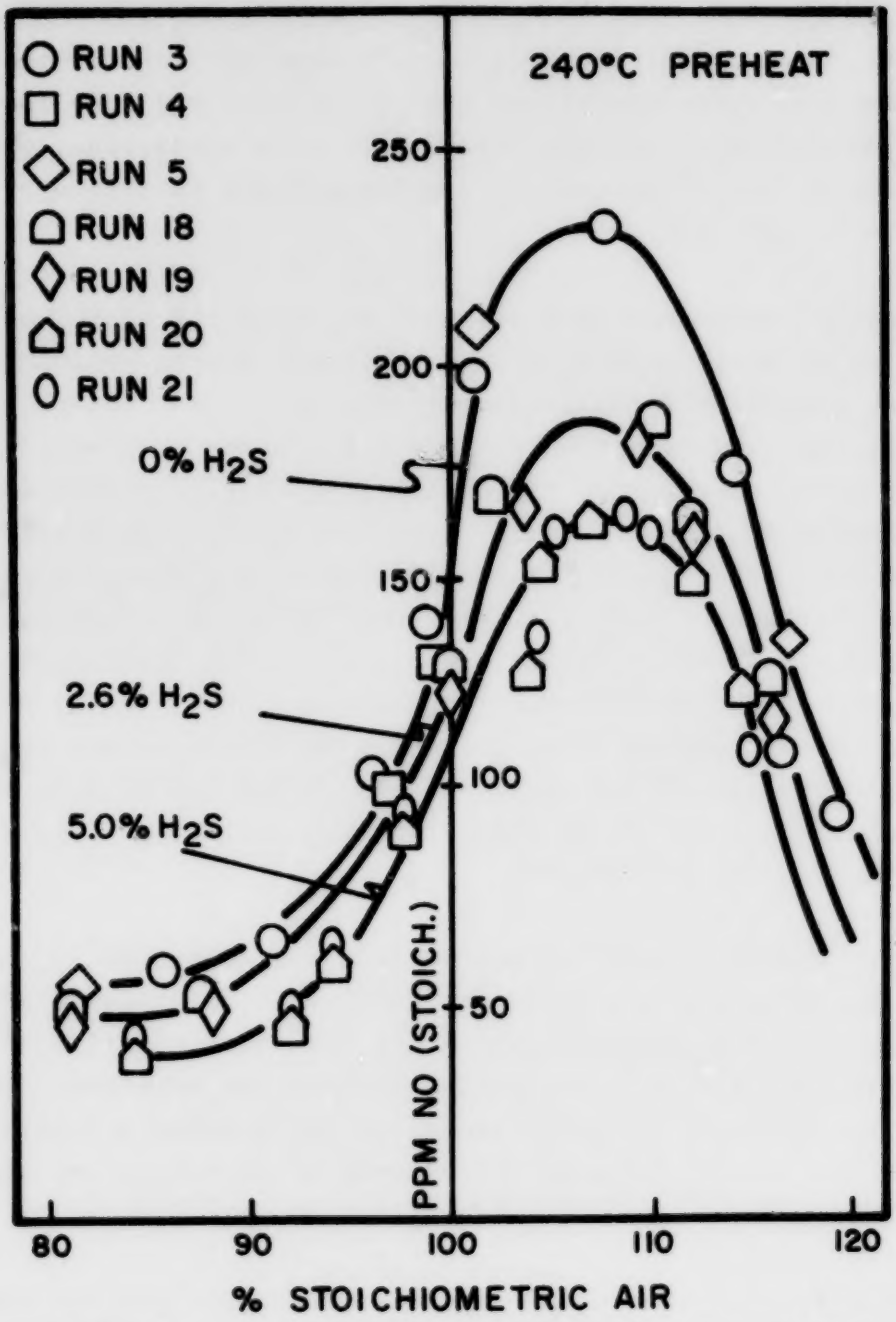

FIGURE 11. H_2S INHIBITS NO FORMATION AT HIGH PREHEAT

up to 31.6% under fuel lean conditions as shown on Table 2. With 250°C mixture preheat, H_2S inhibits NO_x formation on the average by an even greater extent as shown on Figure 11 and Table 2.

Figure 12 shows the effect of H_2S on "prompt NO", and indicates that under fuel lean conditions the presence of H_2S does lower "prompt NO" formation rates. Under fuel rich conditions, where conversion of H_2S to SO_2 is not complete, there is little effect of H_2S on "prompt NO".

The foregoing indicates that H_2S must be converted to SO_2 before inhibition of NO is important, and that this occurs rapidly under fuel lean conditions. This is confirmed in Figures 13 and 14 in which SO_2, NO, and O_2 concentrations are plotted as functions of time for zero preheat. At 98% stoichiometric air (Figure 13) H_2S conversion to SO_2 is essentially complete when NO has attained 70% of its final value; at 113.5% stoichiometric air the conversion of H_2S to SO_2 is essentially complete when the NO has attained only 34% of its final value. Since H_2S has a greater inhibiting effect in the fuel lean case, it would appear that inhibition of NO formation occurs through the rapid conversion of H_2S to SO_2 and by the subsequent inhibiting effect of SO_2. Thus, under fuel lean conditions, a kinetic model simulating fuel sulfur as SO_2, rather than as H_2S, would be adequate.

PHASE II. EFFECT OF FUEL SULFUR ON FUEL NO_x EMISSIONS

In this phase of the research, the effect of the presence of sulfur compounds in a gaseous fuel on the formation of nitrogen oxides arising from fuel nitrogen oxidation was examined. The problem is important because removal of sulfur from a fossil fuel does not necessarily lead to the removal of an equivalent amount of fuel nitrogen.

Unfortunately, our results are somewhat contradictory and some further work is required to reconcile some of the discrepancies discussed below. Experimental difficulties were encountered in

Table 2. REDUCTION IN NO_x EMISSIONS BY H S ADDITION TO FUEL

Percent Stoichiometric Air	Reduction in NO_x Emissions							
	2.6% H_2S in Fuel				5.0% H_2S in Fuel			
	no preheat		240°C preheat		no preheat		240°C preheat	
	ppm	%	ppm	%	ppm	%	ppm	%
80	5.0	11.4	7.0	13.2	5.0	11.4	13.0	24.6
90	8.0	14.6	10.0	15.4	8.0	14.6	20.0	30.8
100	28.0	23.3	26.0	17.1	28.0	23.2	42.0	27.7
103	17.0	11.4	50.0	22.8	28.0	18.9	75.0	34.0
110	15.0	11.1	44.0	19.1	26.0	19.4	63.0	28.0
115	15.0	15.8	23.0	14.1	30.0	31.6	48.0	29.4

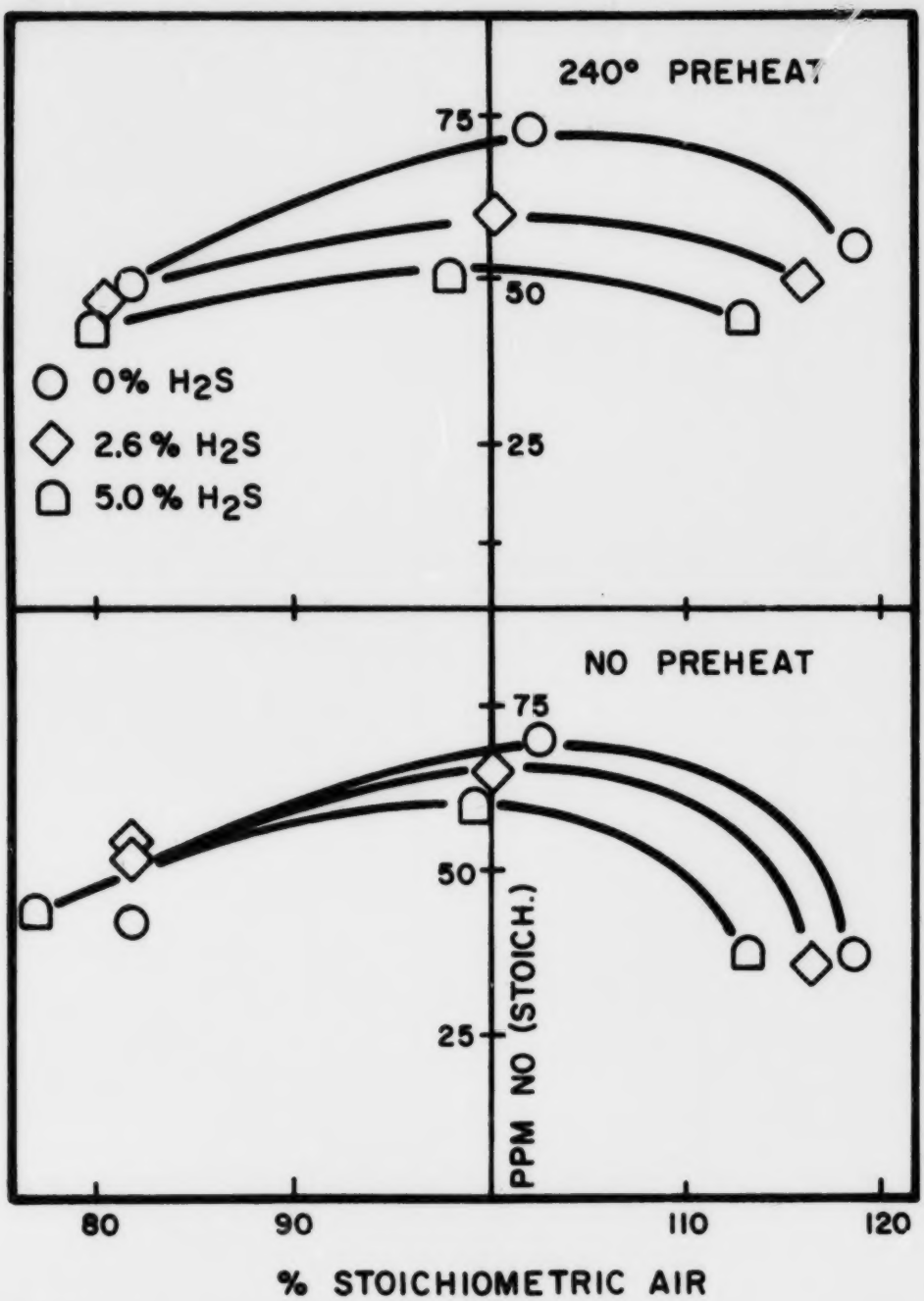

FIGURE 12. EARLY-FORMED NO INHIBITED BY H_2S

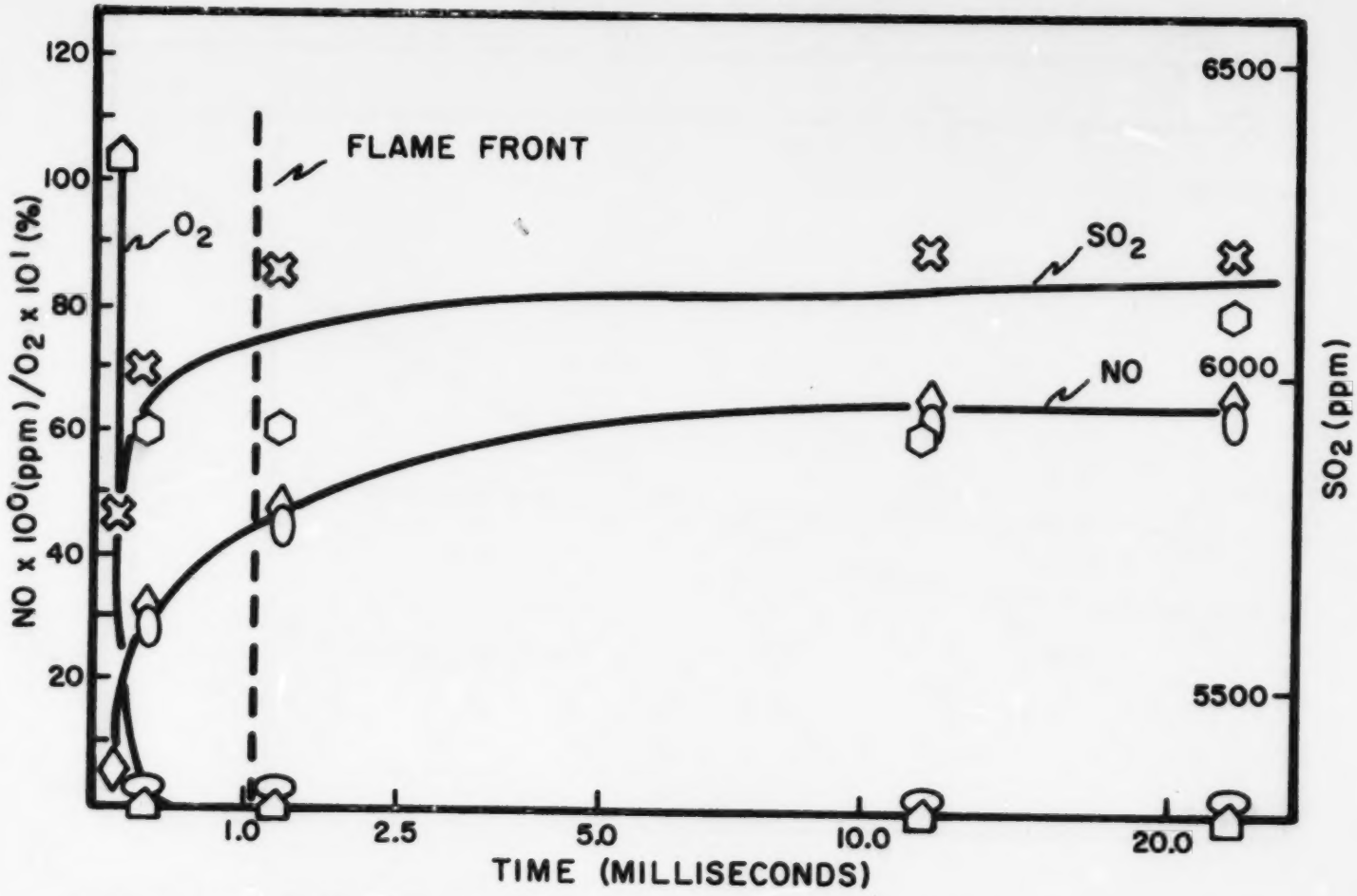

FIGURE 13. CONVERSION OF H_2S TO SO_2 IS MORE RAPID THAN NO FORMATION-FUEL RICH CONDITIONS

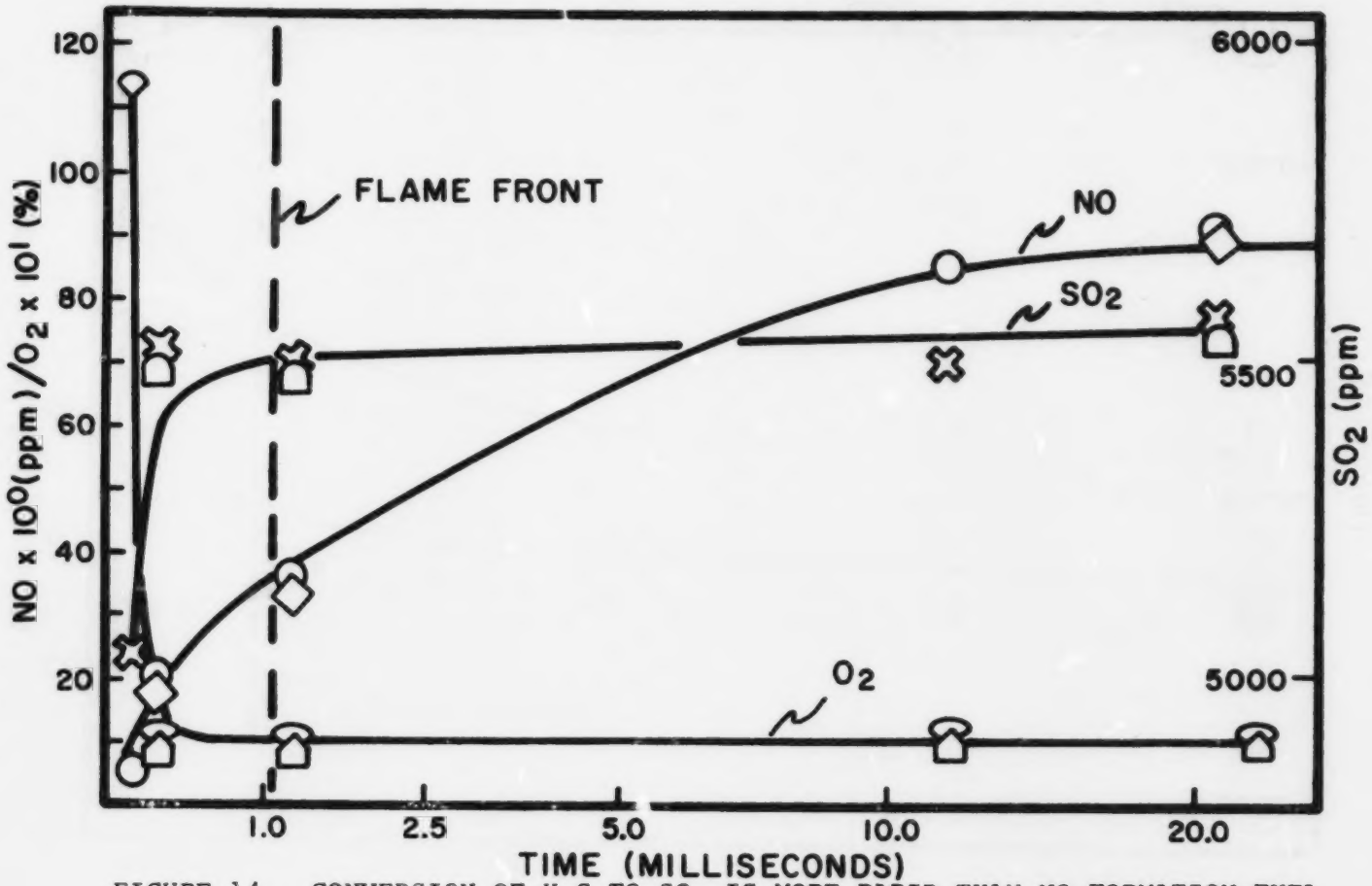

FIGURE 14. CONVERSION OF H_2S TO SO_2 IS MORE RAPID THAN NO FORMATION-FUEL LEAN CONDITIONS

reproducing exact same fuel nitrogen additive flow rates from one day to the next, although within any one experimental run, additive flow rates were maintained constant. Nitrogen oxide emission are, of course, very sensitive to the quantity of fuel nitrogen added to the flame. It should be emphasized, therefore, that the results from Phase II, are preliminary in nature. They are reported here because they appeared to indicate the presence of new, interesting and reproducible phenomena, when both fuel sulfur and fuel nitrogen are present in a flame. When viewed in this light, the results are valuable, since they provide impetus for further investigation.

The research can be divided into two separate experimental trials. In the first trial the concentration of nitric oxide (NO) was measured as a function of distance from the burner grid for various air fuel ratios with and without sulfur dioxide added to the fuel. The fuel was doped with NO to simulate fuel nitrogen. In this trial the flame was detached from the burned grid and this allowed probing well into the flame front.

In the second trial, the combustor was modified to allow greater ease of operation. The modifications caused the flame to burn partially upstream of the grid surface, thus preventing any probing well into the flame front. This difference in flame behavior between the first and second trials, might explain apparent discrepancies between results from these trials. In the second trial, NO, NO_x, SO_2 and CO were measured in all runs. A Molybdenum converter was used to convert NO_2 to NO under fuel rich conditions. The fuel was doped with both NO and with C_2N_2 to simulate fuel nitrogen.

PHASE II. TRIAL 1

Concentration profiles of NO are shown for three stoichiometric ratios on Figures 15 through 17. Fuel nitrogen was simulated by addition of NO in the fuel. Since some NO oxidized to NO_2 before reaching the burner grid the inlet values of NO and NO_x are

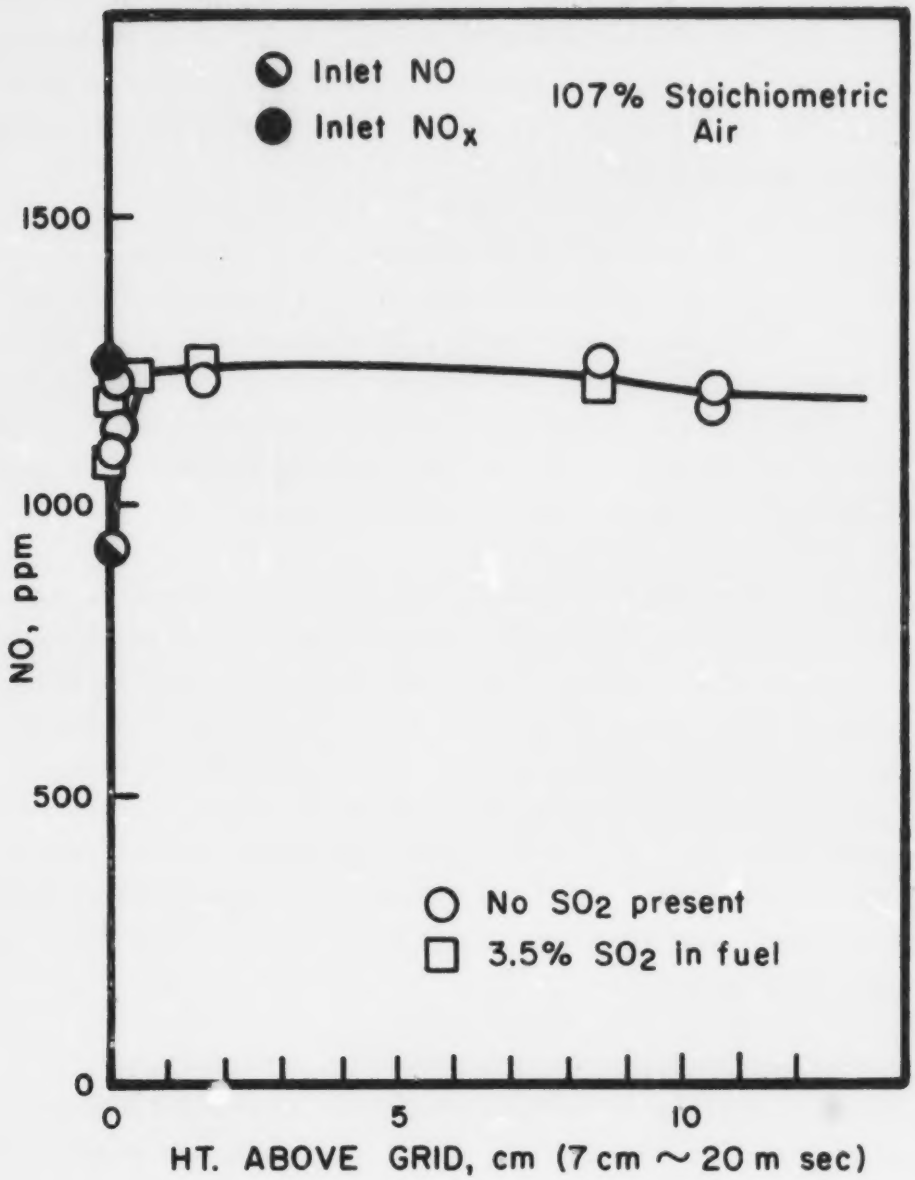

FIGURE 15. EFFECT OF SO_2 on FUEL NO UNDER FUEL LEAN CONDITIONS

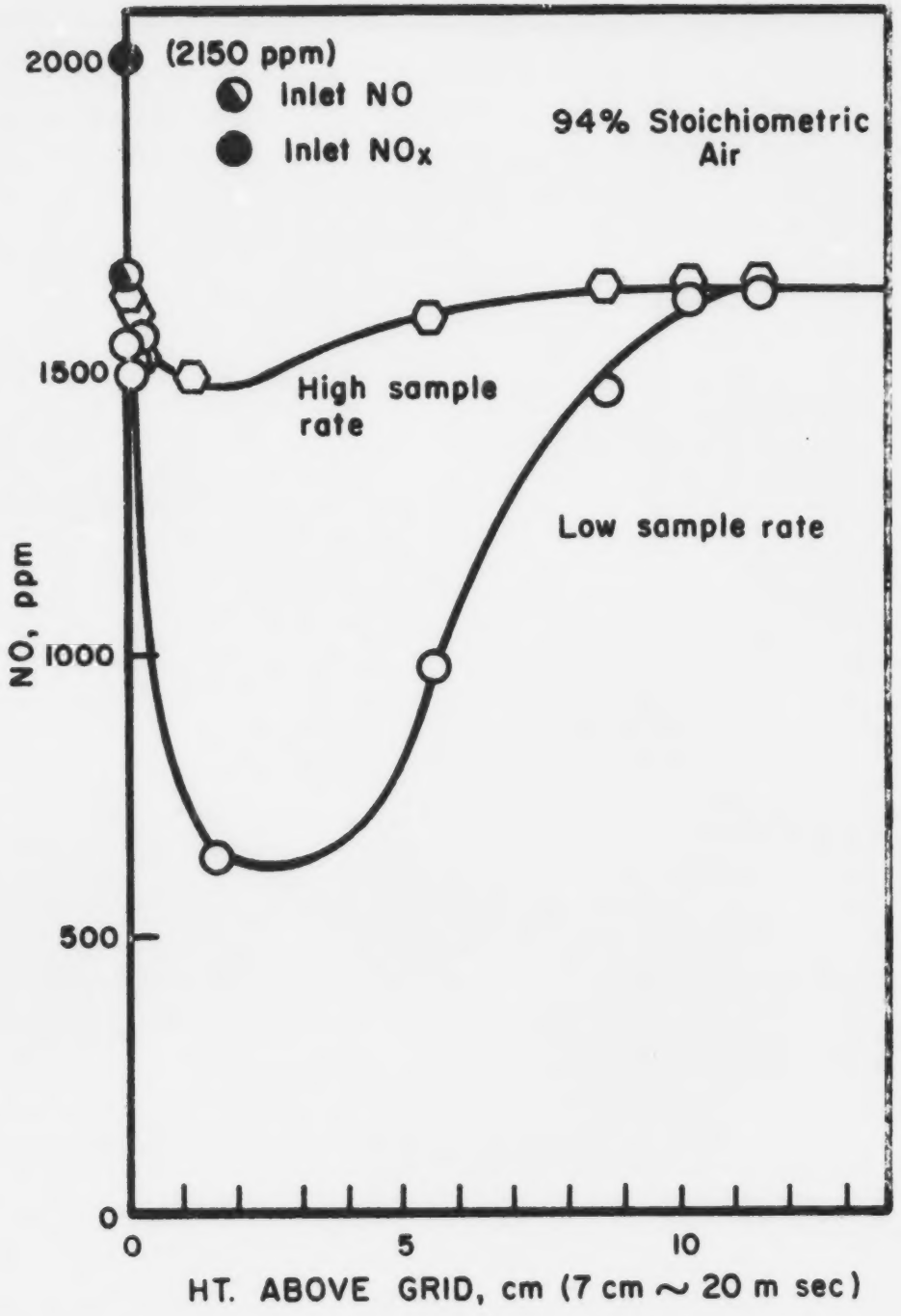

FIGURE 16. EFFECT OF SAMPLING RATE ON FUEL UNDER FUEL RICH CONDITIONS

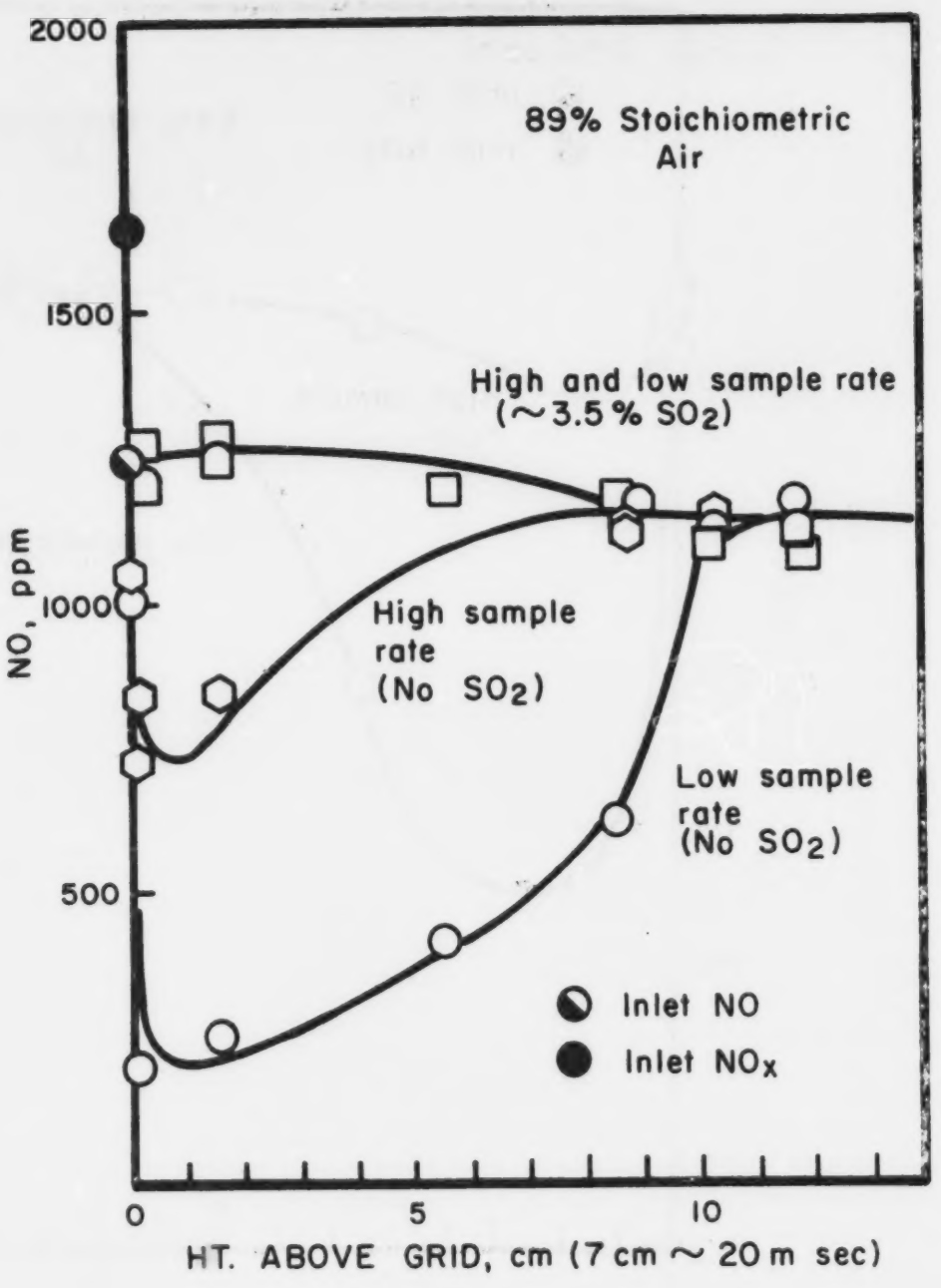

FIGURE 17. EFFECT OF SO_2 AND SAMPLING RATE ON NO PROFILES

those measured leaving the grid in the absence of a flame. Figure 15 shows results under fuel lean conditions. The presence of SO_2 in the fuel had essentially no effect on the NO profile. Figure 16 shows the concentration profile of NO under fuel rich conditions. A rapid decline in apparent NO concentrations was followed by a very slow increase. This was unexpected, and so the sampling rate through the uncooled quartz probe was varied in order to determine if probe effects were controlling. Results on Figure 16 indicate that under our conditions reactions in the probe were apparently destroying NO, but that these reactions do not occur when the sample is withdrawn far from the flame front. Figure 17 shows NO concentration profiles under fuel rich conditions, with and without SO_2 present (3.5% SO_2 in the fuel) and at high and low sampling rates. The following observations can be made. First, in the absence of SO_2, the same basic trends as shown in the previous figure were observed. Second, SO_2 markedly affected the apparent NO profile, although exhaust values did not change significantly. Third, with SO_2 present there appeared to be little effect of sampling rate. However, it should be noted that neither the presence of SO_2 nor sample rate had an effect on exhaust values of NO.

PHASE II: TRIAL 2

Trial 2 was completed after substantial modifications to the burner had been made. These modifications were necessary because of wear and tear on the original combustor. It was hoped to explore the results of Trial 1 in more detail; however, it became quickly apparent that the combustor performance in Trial 2 was quite different and that this led to significant qualitative differences between results of the two Trials. An important difference between the two combustors was that in the latter trial, the stable flame was seated in and below the grid, while before it was lifted several millimeters above the grid. The results of the trials should therefore be viewed as results from different combustors. In Trial 2 both NO and cyanogen were added to the fuel and both NO and NO_x were measured. The effects of SO_2 and

sampling rate were investigated. Results are shown in Figures 18 through 21.

Figure 18 shows concentration profiles for NO addition with and without SO_2 addition under fuel lean conditions. Sample rates were not changed. Essentially no significant effect was observed, and these data are in agreement with those from Trial 1. The small decrease in NO due to the presence of SO_2 is probably due to thermal fixation effects investigated in Phase 1.

In Figure 19 the concentration profiles are shown for the case where cyanogen was used to simulate the fuel nitrogen compound. Conversion of cyanogen to NO was close to 100%. These data agree with those of DeSoete[17]. No effect of sampling rate was observed.

Figures 20 (NO addition) and 21 (C_2N_2 addition) show concentration profiles of NO and NO_x under fuel rich conditions. It is immediately clear that these data differ substantially from those of Trial 1, in that exhaust values of NO and NO_x are achieved much more rapidly. Indeed, in Trial 2, the rapid decrease of NO to very low values, in the flame front, was observed only with difficulty. This was because the flame front extended to behind the grid. From Figure 20 (NO addition) one can deduce that, in the flame front region, the apparent values of both NO and NO_x did depend on sampling rate, while with SO_2 present, they did not. Exhaust values were essentially unaffected. With C_2N_2 as the fuel nitrogen additive, the data (Figure 21) show that sampling rate did have an effect on NO and NO_x in the flame front both with and without SO_2. In addition, SO_2 tended to decrease the exhaust emissions of NO_x by about 400 ppm. This is a new phenomenon, and should be examined further.

Reproducibility of data shown in Figures 18 through 21 was good, and many overlapping points have not been shown in order to im-

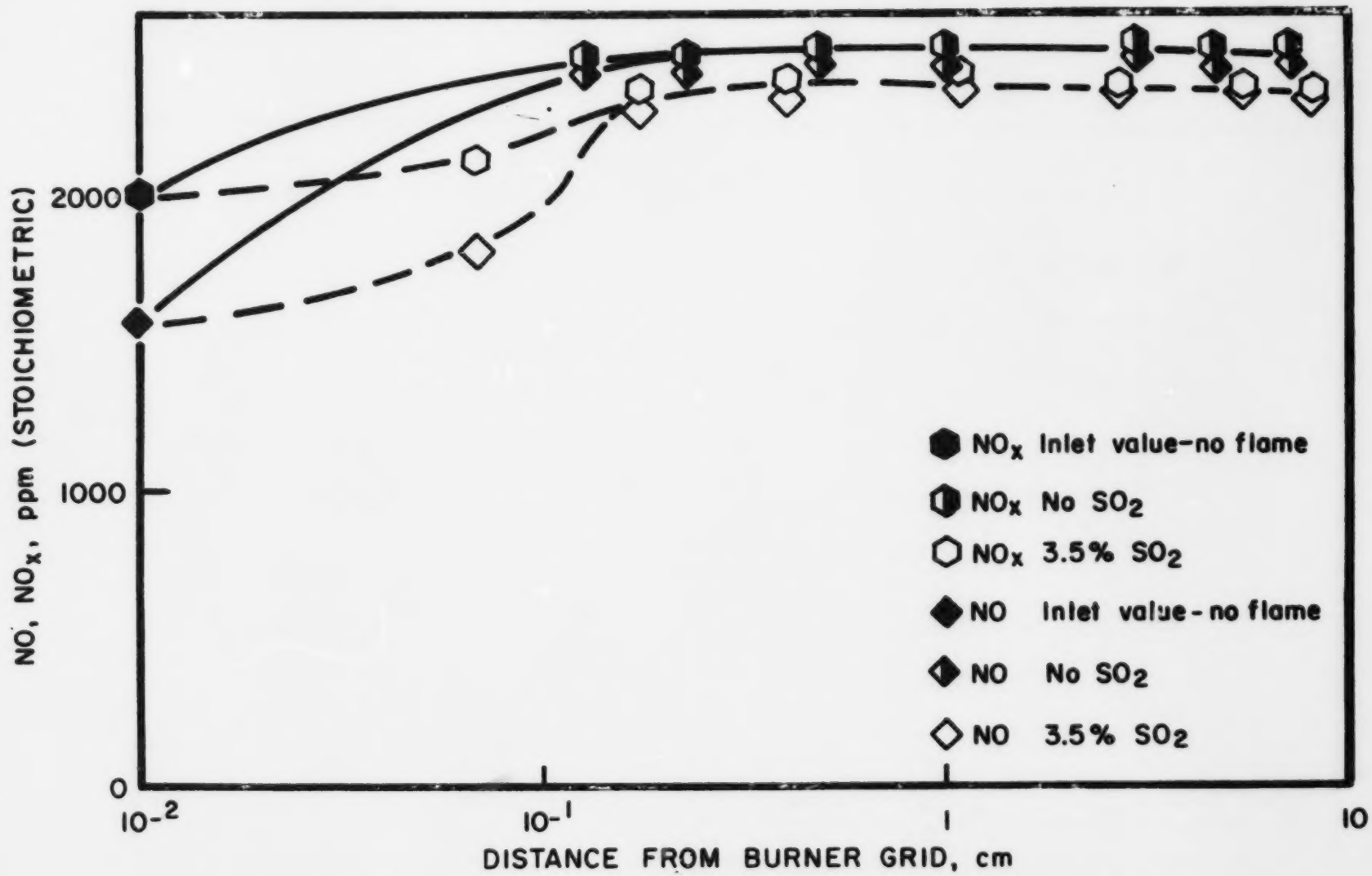

FIGURE 18. EFFECT OF SO_2 ON NO, NO_x, PROFILES, (FUEL NITROGEN = NO, 107% STOICHIOMETRIC AIR)

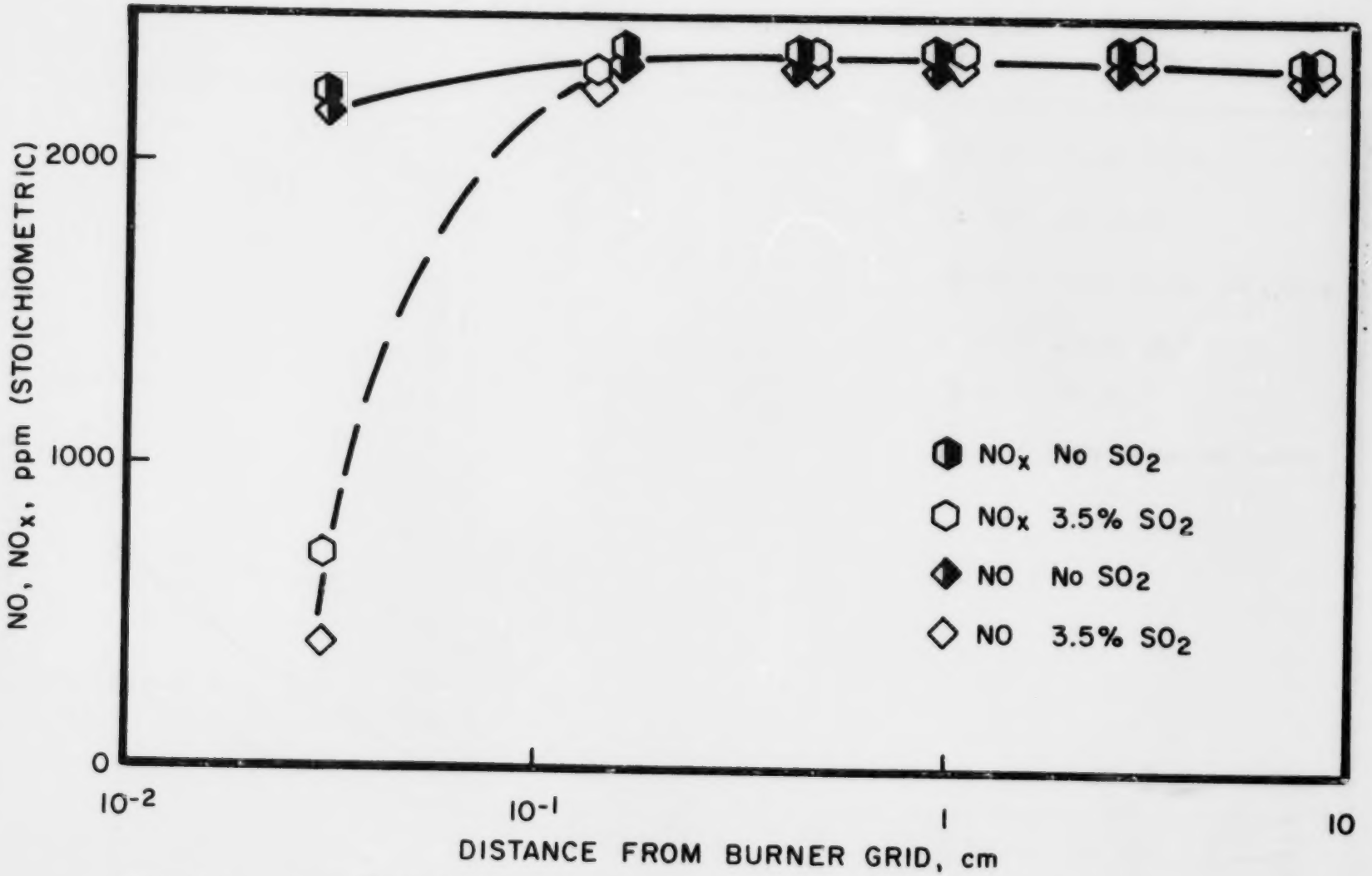

FIGURE 19. EFFECT OF SO_2 ON NO, NO_x PROFILES (FUEL NITROGEN = C_2N_2, 107% STOICHIOMETRIC AIR)

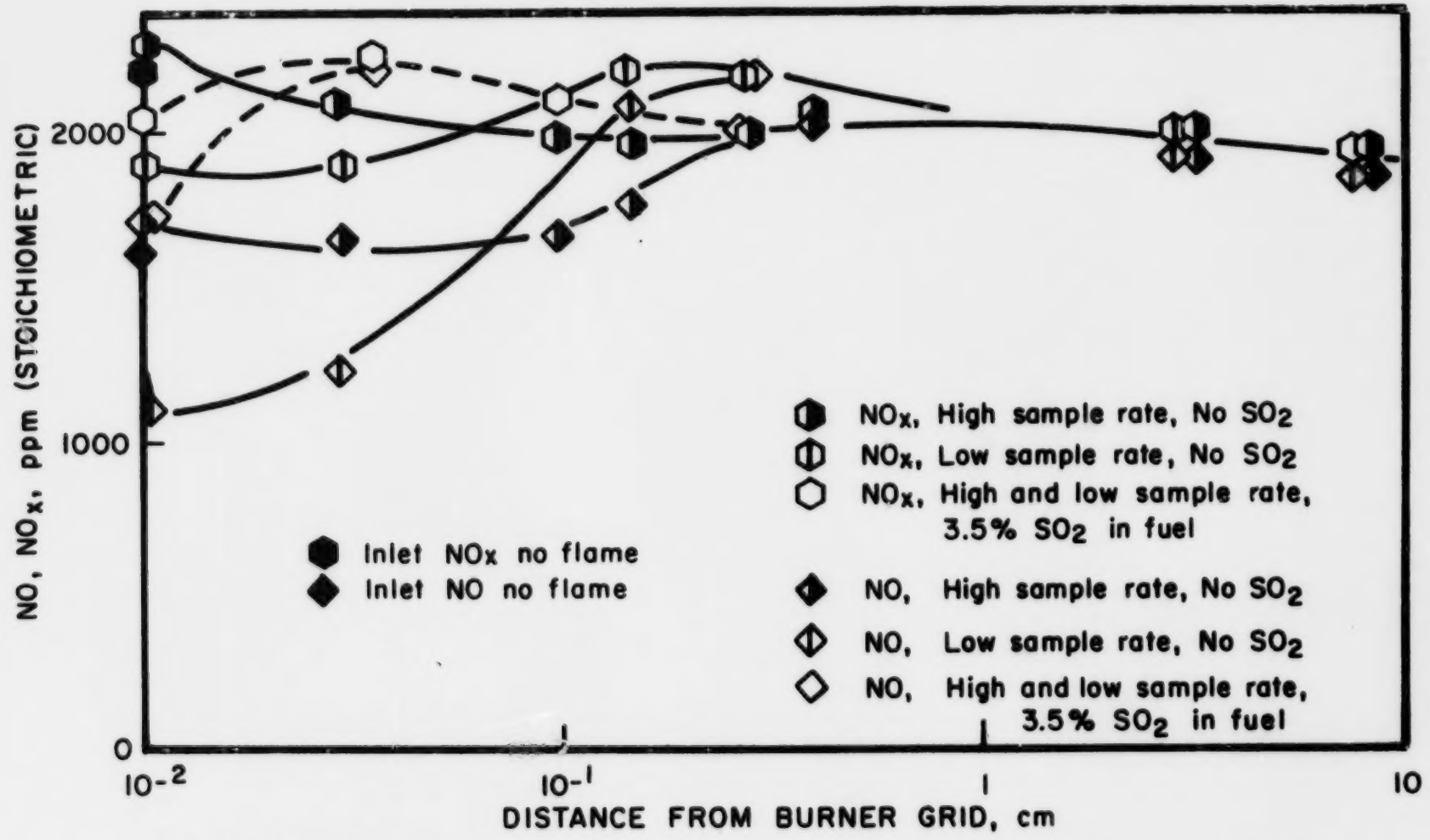
NO, NOx, ppm (STOICHIOMETRIC)
2000
1000
0
10-2
10-1
1
10
DISTANCE FROM BURNER GRID, cm
Inlet NOx no flame
Inlet NO no flame
NOx, High sample rate, No SO2
NOx, Low sample rate, No SO2
NOx, High and low sample rate, 3.5% SO2 in fuel
NO, High sample rate, No SO2
NO, Low sample rate, No SO2
NO, High and low sample rate, 3.5% SO2 in fuel

FIGURE 20. EFFECT OF SO_2, SAMPLING RATE ON NO, NO_X, PROFILES, (FUEL NITROGEN = NO, 89% STOICHIOMETRIC AIR)

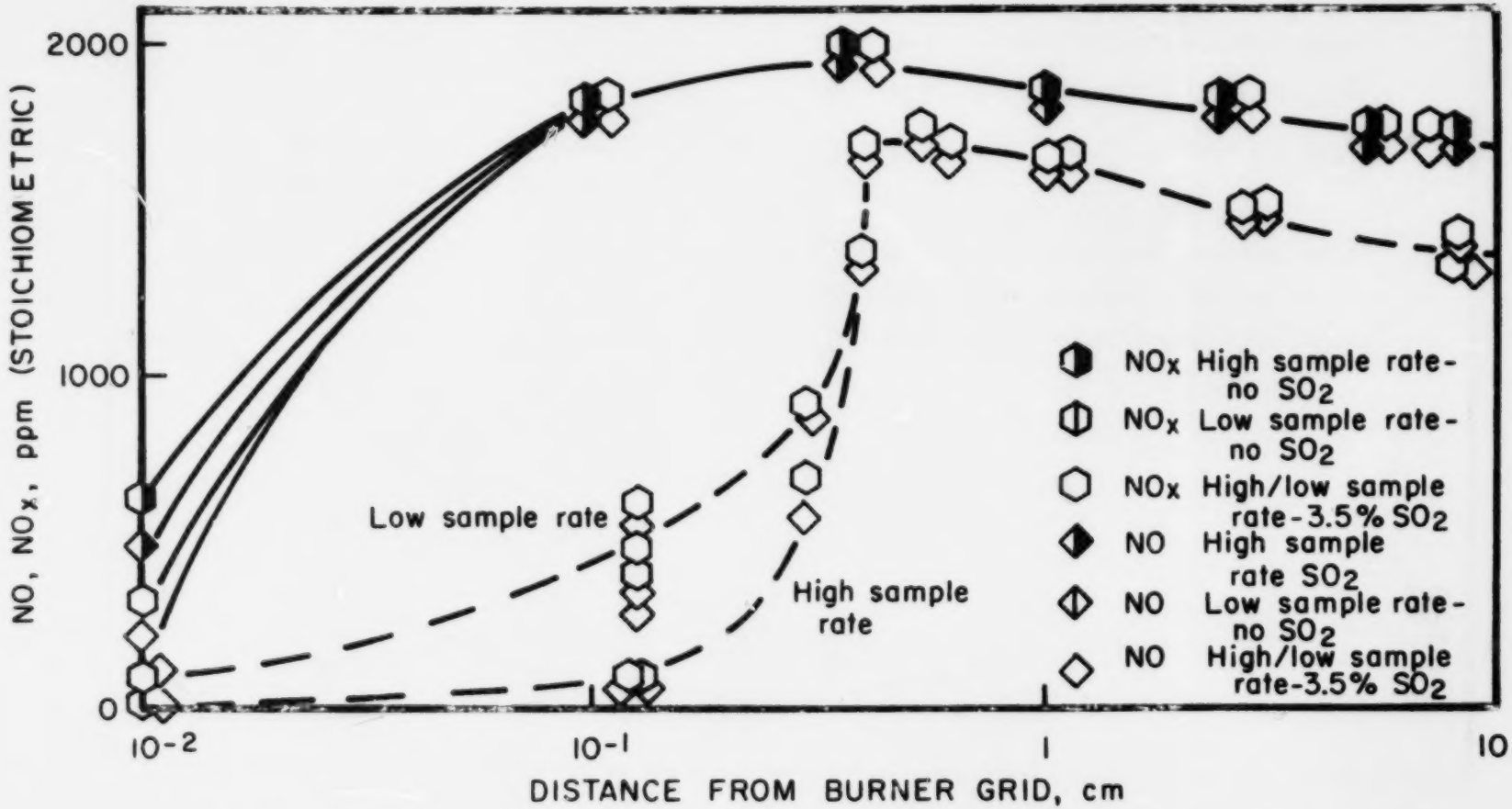

FIGURE 21. EFFECT OF SO_2, SAMPLING RATE ON NO, NO_x PROFILES (FUEL NITROGEN = C_2N_2, 89% STOICHIOMETRIC AIR)

prove clarity. In each case SO_2 concentrations were measured, and showed that under fuel rich conditions SO_2 was reduced slightly in the flame front, and then restored back to its original value. It should be noted that inlet values of NO and NO_x were measured in the absence of combustion, and therefore in the absence of water vapor. The actual inlet values of NO and NO_x during combustion would be somewhat higher. The species concentrations reported are on a dry basis and reduced to stoichiometric conditions. For the purposes of this calculation it was assumed that all unburned fuel was in the form of CO. A logarithmic abscissa scale was used in Figures 18 through 21 in order to allow an expanded scale in the flame front region.

MATHEMATICAL MODELING

In order to model the kinetic mechanisms of the sulfur-nitrogen oxide interactions experimentally observed it is first necessary to model the physical environment of a flat flame in which the reaction chemistry occurs. In a flat flame the physical processes of convection and diffusion are important and simple plug flow models are inadequate. Indeed a substantial amount of back diffusion into the unburned gases is crucial in allowing a stable flame front to be maintained, and in allowing ignition to occur. Simple models that impose a specified time temperature-history on the kinetics environment can be misleading, especially in the case examined here, where temperature, free radical concentrations and nitrogen oxide kinetics are intimately coupled. For example, high superequilibrium concentrations of atoms and free radicals necessarily lead to significantly lower temperatures because of the enthalpy of disassociation of oxygen, hydrogren and water molecules. Thus a substance that catalyzes atom recombination rates and lowers free radical concentrations, will also raise the flame temperature at that point and this rise in temperature may offset, in some degree, the effect of lower oxygen atom concentrations as regards NO formation. Thus any reasonable model describing the observed effects must

a) calculate the resulting temperature from a heat balance and

b) properly take account of diffusion in the flame front

Unfortunately, no model of a flat flame is generally available and so it was necessary to develop a very approximate simulation

to be used in this study. It is recognized that substantial improvements in such a simulation are desirable; however, our model is an improvement on others that take no account of diffusion in the flame front. The approach used here was to develop a simplified premixed flat flame model that takes account of diffusion, then to calibrate this model against

a) literature data on free radical concentrations and

b) our own base case of NO formation without sulfur present

It should be noted that the model therefore used only two unknown parameters, one of which was obtained from the open literature, the other of which uses our own base case data. This model was then used to test kinetic mechanisms of sulfur oxide - nitrogen oxide interactions, and the resulting mechanism was then used to determine the effect of different environments and different heat loss rates corresponding to those likely in a furnace.

PREMIXED FLAT FLAME MODEL

The salient features of our preliminary flat flame model is that the diffusion in the ignition zone is assumed to be such that it can be simulated by a well stirred stage or pointwise calculation. This simulation is exact[18] only when the true profiles are parabolic and since this is seldom the case, the model should be considered only an approximate representation of our flat flame. The ignition zone is then followed by a plug flow calculation. The volume of the (hypothetical) well stirred stage is determined by that which allows a certain fraction of a species (designated "fuel") to be destroyed. The physical assumption is, that for a given fuel, the correct scaling parameter is a quantity related to the flame thickness, and that this length can be determined by the concentration profile of the species designated as "fuel". The model, at this stage, is largely intuitive, and should be regarded merely as a mathematical device to simulate ignition. A rigorous mathematical justification of this approach is outside

the scope of this phase of the project. Here we will merely demonstrate that the model does predict atom concentrations of the correct order as those measured[19] and this gives us some confidence that the model can describe the pheomena of interest here.

The basic tool used was computer program REKINET which integrates the conservation equations for well stirred and plug flow reactors both with and without a heat balance. In addition, this program allows the volume of the well stirred stage to vary until a specified fraction of a specified species is converted.

The basic approach used to model the flat flame investigated here consisted of the following steps:

- choose a kinetic mechanism for CH_4/air combustion
- determine which value of percent CH_4 consumed (denoted by χ) during pointwise calculation led to measured oxygen atom concentrations of Peeters and Mahnen[19]
- use this value of χ to simulate our flat flame and calibrate the heat loss parameters in the model until the predicted and measured base case NO profiles matched
- investigate changes due to SO_2 addition, assuming atom recombination catalysis with mechanisms and rates proposed by Halstead and Jenkins[5] and Merryman and Levy[20]. No other parameters should be altered in this phase.

KINETIC MECHANISM

The methane air reactions used were those suggested by Waldman *et al.*[4] in an EPA sponsored investigation of kinetic mechanisms of methane/air combustion with pollutant formation. A list of reactions is shown on Table 3. The reactions name ULT36 through ULT143 denote the reactions numbered 36 through 143 in Table 7.5 of Reference (4). Special consideration is made of catalysis of atom recombination rates through O_2, forming HO_2 as an intermediate - see reactions ULT101 and ULT85.

Table 3. METHANE COMBUSTION MECHANISM

ULT36	CHO	+M		=CO	+H	+M
ULT77	CO2	+M		=CO	+O	+M
ULT84	H20	+M		=OH	+H	+M
ULT99	H	+O	+M	=OH	+M	
ULT101	H	+O2	+M	=HO2	+M	
ULT140	N20	+M		=N2	+O	+M
ULT44	CHO	+H		=CO	+H2	
ULT46	CH20	+O		=CHO	+OH	
ULT47	CHO	+OH		=CO	+H2O	
ULT52	CHO	+O		=CO	+OH	
ULT59	CH3	+O		=CH2O	+H	
ULT63	CH4	+O		=CH3	+OH	
ULT65	CH4	+H		=CH3	+H2	
ULT66	CH4	+OH		=CH3	+H20	
ULT70	CO	+OH		=CO2	+H	
ULT83	H	+OH		=H2	+O	
ULT85	H	+HO2		=OH	+OH	
ULT88	OH	+H2		=H	+H2O	
ULT91	OH	+N		=H	+NO	
ULT98	H	+N2O		=OH	+N2	
ULT100	OH	+O		=H	+O2	
ULT117	OH	+OH		=H2O	+O	
ULT125	N	+NO		=N2	+O	
ULT133	N	+O2		=NO	+O	
ULT135	N2O	+O		=NO	+NO	
ULT143	CHO	+O2		=CO	+HO2	
JOHN11	O2	+M		=O	+O	

In addition, for the runs simulating sulfur addition, the atom recombination catalysis is described by reations shown in Table 4. Those reactions named MERL1 and MERL3A are reactions numbered 1 and 3A by Merryman and Levy[20] while those labeled JENKI are from Halstead and Jenkins[5]. Reaction JOHN11 is from Johnston's review of O atom kinetics[21].

These reactions demonstrate the catalysis of O atom recombination by SO_2 via SO_3 as an intermediate as well as the catalysis of H atom and OH radical recombination to form H_2O, with HSO_2 as an intermediate. No adjustment of rate coefficient values from those suggested by the original authors was made and it was assumed throughout that:

$$k_{f/k_r} = K_{equil}$$

An important result obtained from this kinetic model is to determine whether this atom recombination catalysis is sufficient to account for the drop in NO emissions caused by SO_2 addition. In addition, a kinetic calculation of this type allows the separate effects of temperature profile changes and radical concentration changes to be investigated. This should lead to greater insight into the salient features involved.

CALIBRATION OF FLAT FLAME SIMULATION WITH DATA OF PEETERS

In our simulation of a flat flame the ignition zone is simulated by a well stirred stage or pointwise calculation where the hypothetical volume is determined by that volume which will convert a certain fraction χ, of the primary fuel. This is followed by a plug flow heat balanced calculation. We settled on a value of χ, of the primary fuel. This is followed by a plug flow heat balanced calculation. We settled on a value of χ by calibrating our simulation with the data of Peeters and Mahnen[18]. Heat loss in the ignition zone was assumed to be negligible. A value of

Table 4. SO_2 CATALYZED RECOMBINATION OF ATOMS AND RADICALS

MERL1	SO2	+O	+M	=SO3	+M
MERL3A	SO3	+O		=SO2	+O2
JENKI1	H	+SO2	+M	=HSO2	+M
JENKI2	HSO2	+OH		=H2O	+SO2

$$\chi = 0.98$$

was chosen because, as shown in Table 5:

- the maximum CH_4 consumption rate was then similar to that measured
- the peak O atom mole fraction (0.048) was of the same order as that measured (0.025) compared to the equilibrium O_2 mole fraction which was two orders of magnitude lower
- the temperature of the hypothetical well stirred stage matched that measured at the maximum CH_4 consumption rate.

The simulation did over predict the atom concentration by a factor of two and also tended to under predict the rate of temperature increase. Obviously the simulation does not give a true picture of the flat flame at this stage, and the discrepancies are probably due to inaccuracies in both the model and the kinetic mechanism. Nevertheless, the simulation was considered sufficiently adequate to investigate the kinetic mechanism appropriate to SO_2 inhibition of nitrogen oxides.

This calculation also demonstrated that the kinetic mechanism of methane combustion proposed by Waldman[4] did contain the salient features observed by Peeters and Mahnen[17]. For example, the predicted formaldehyde, hydroxyl and carbon monoxide profiles were reasonably close to those measured. This gives both the kinetic mechanism and the simulation some credence.

CALIBRATION WITH BASE CASE NO MEASURED

The base cases used to test the kinetic model were those with 104% stoichiometric air at both zero and 240°C mixture preheat. We restricted our investigation to the fuel lean regime because the dominant NO formation kinetics are there better understood. Using the value of $\chi = 0.98$ determined previously and the kinetic mechanism for methane combustion shown on Table 3 it was found

Table 5. SIMULATION OF FLAME OF PEETERS *et al.* (1973)

	Simulation	Experiment
Temperature at Ignition Zone Exit, °K	1569	1550
Max. Rate of CH_4 Consumption, moles/cc sec	5.53×10^{-5}	8.4×10^{-5}
Ignition Zone Exit, Mole Fractions		
CO	0.0336	0.042
O	0.0343	0.011
OH	0.0173	0.015
CH_2O	0.00126	0.001
Max. O Atom Mole Fraction	0.0474	0.025

that the NO measurements in our flat flame could be matched by the simulation with a radiative heat loss coefficient

$$\sigma = 3.45 \times 10^{-14} \quad \text{cal/sec cm}^3\ ^\circ\text{K}^4$$

for the case with no preheat, and with

$$\sigma = 8.0 \times 10^{-14} \quad \text{cal/sec cm}^3\ ^\circ\text{K}^4$$

for the case with 240°C mixture preheat.

The discrepancy between these two values indicate shortcomings in our model. However, since the purpose of our model is to predict the change in NO due to SO^2 addition, it is reasonable to calibrate against both the zero and high preheat base cases individually. Obviously an improved model should be able to predict the effect of mixture preheat, without additional calibration.

EFFECT OF SO_2 IN FUEL

With 4.9% SO_2 in the fuel the simulation showed a drop of 49 ppm NO in the exhaust for the case with no preheat. This compares with a measured drop of 40 ppm as shown in Table 6. At 240°C preheat the simulation predicted a drop of 51 ppm NO compared to a measured reduction of 70 ppm. Given the inaccuracies of the physical model, and the kinetic rate coefficients, the simulation predicts the correct effect of SO_2 addition with remarkable accuracy, especially for the no preheat case. The discrepancy between theory and experiment in the high preheat case may be due to an inaccurate simulation of the heat loss under that condition. It is clear, therefore, that the SO_2 catalysis of atoms and free radicals as described by Reactions MERL1 through JENKI2 on Table 4 can explain the observed inhibition NO formation by SO_2.

ANALYSIS OF SIMULATION AND APPLICATION

Calculated profiles of oxygen atom concentration, NO concentration

Table 6. EFFECT OF SO_2 ON NO_x EMITTED: SIMULATION AND MEASURED VALUES

	Simulation	Measured
Base case, 104% stoich. air, zero preheat, NO ppm	148	150
4.9% SO_2 in fuel, NO PPM	99	110
Reduction in NO ppm	49	40
Percent reduction in NO	33	27
Base case, 104% stoich. air, 240°C preheat, NO ppm	232	232
4.9% SO_2 in fuel, NO ppm	181	160
Reduction in NO ppm	51	72
Percent reduction in NO	22	30

and temperature are shown on Figure 22 for the zero preheat case. It is clear that the addition of SO_2 to the fuel changes both the oxygen atom and the temperature profiles (assuming that the radiative heat transfer coefficient remains unchanged). In the presence of SO_2 the higher temperature at early times is intimately coupled with the drop in atom concentration, which is significant. This indicates that before 10^{-4} seconds the NO formation rate is actually slightly higher with SO_2 than with no SO_2. However, during the time when most of the NO is being formed and when radiative heat loss is important, the drop in O atom concentration dominates, and the resultant NO formed is significantly lower. It is clear, therefore, that the reason behind the observed effect is that the presence of SO_2 catalyzes the recombination of oxygen atoms, and that the drop in oxygen atom concentration is sufficient to lower the NO formation rate.

There is, however, a qualitative discrepancy between the predicted profile of NO shown on Figure 22 and that measured (at a different air/fuel ratio) and shown on Figure 8. In general, the measured profile showed a more rapid formation of prompt NO than that predicted. This qualitative discrepancy is probably due to unknown features in the mechanism of prompt NO formation. It is felt, however, that this discrepancy is not serious and does not detract from the point that O atom recombination catalysis by SO_2 can explain the drop in exhaust NO measured, with no adjustment to known rate coefficients being necessary. Further details of the results from the model are shown on Table 7 for the no preheat case and Table 8 for the high preheat case. These tables show the early formation of superequilibrium concentrations of SO_2, which is an intermediate species in the recombination catalysis scheme, followed by a decline to relatively low values, corresponding to approximately 1% conversion of SO_2 to SO_3. Surprisingly, the calculations also indicate that the addition of SO_2 also appears to hasten the CO burnout rate, although low CO levels were obtained in all cases.

Table 7. SIMULATION DETAILS - NO PREHEAT

	Mole Fractions				Temp.
Time(sec)	NO	O	SO_3	CO	T°K
0% SO_2 in Fuel					
Ignition Zone Exit	0.479E-7	0.458E-2	--	0.408E-1	1659
0.11×10^{-5}	0.488E-7	0.484E-2	--	0.414E-1	1678
0.125×10^{-4}	0.720E-7	0.555E-2	--	0.364E-1	1754
0.482×10^{-4}	0.253E-6	0.465E-2	--	0.267E-1	1850
0.133×10^{-3}	0.112E-5	0.343E-2	--	0.216E-1	1935
0.329×10^{-3}	0.404E-5	0.236E-2	--	0.183E-1	2003
0.780×10^{-3}	0.118E-4	0.158E-2	--	0.151E-1	2055
0.140×10^{-2}	0.223E-4	0.119E-2	--	0.129E-1	2081
0.365×10^{-2}	0.537E-4	0.749E-3	--	0.979E-2	2099
0.996×10^{-2}	0.103E-3	0.454E-3	--	0.686E-2	2064
0.280×10^{-1}	0.140E-3	0.197E-3	--	0.338E-2	1939
0.425×10^{-1}	0.145E-3	0.119E-3	--	0.208E-2	1852
4.9% SO_2 in Fuel					
Ignition Zone Exit	0.622E-7	0.396E-2	0.384E-3	0.400E-1	1686
0.104×10^{-5}	0.632E-7	0.415E-2	0.387E-3	0.406E-1	1704
0.118×10^{-4}	0.883E-7	0.466E-2	0.325E-3	0.362E-3	1783
0.347×10^{-4}	0.204E-6	0.386E-2	0.221E-3	0.286E-1	1864
0.298×10^{-3}	0.388E-5	0.158E-2	0.321E-4	0.154E-1	2046
0.723×10^{-3}	0.106E-4	0.994E-3	0.136E-4	0.118E-1	2094
0.123×10^{-2}	0.178E-4	0.755E-3	0.887E-5	0.100E-1	2113
0.303×10^{-2}	0.377E-4	0.480E-3	0.519E-5	0.704E-2	2123
0.835×10^{-2}	0.701E-4	0.282E-3	0.425E-5	0.494E-2	2090
0.123×10^{-1}	0.819E-4	0.212E-3	0.438E-5	0.389E-2	2058
0.256×10^{-1}	0.956E-4	0.903E-4	0.534E-5	0.180E-2	1959
0.372×10^{-1}	0.978E-4	0.457E-4	0.650E-5	0.916E-3	1882

Table 8. SIMULATION DETAILS - 240°C PREHEAT

Time(sec)	Mole Fractions NO	O	SO_3	CO	Temp. T°K
0% SO_2 in Fuel					
Ignition Zones Exit	0.129E-6	0.[illegible]2	--	0.440E-1	1745
0.4×10^{-6}	0.131E-6	0.[illegible]E-2	--	0.443E-1	1754
0.11×10^{-4}	0.196E-6	0.721E-2	--	0.394E-1	1836
0.4×10^{-3}	0.168E-4	0.271E-2	--	0.208E-1	2124
0.158×10^{-2}	0.748E-4	0.149E-2	--	0.154E-1	2175
0.47×10^{-2}	0.164E-3	0.891E-3	--	0.111E-1	2133
0.16×10^{-1}	0.226E-3	0.315E-3	--	0.491E-2	1947
0.22×10^{-1}	0.230E-3	0.202E-3	--	0.325E-2	1858
4.9% SO_2 in Fuel					
Ignition Zone Exit	0.169E-6	0.539E-2	0.306E-3	0.432E-1	1773
0.5×10^{-6}	0.171E-6	0.549E-2	0.307E-3	0.436E-1	1785
0.11×10^{-4}	0.260E-6	0.613E-2	0.237E-3	0.384E-1	1875
0.3×10^{-3}	0.128E-4	0.220E-2	0.175E-4	0.191E-1	2147
0.179×10^{-2}	0.769E-4	0.982E-3	0.528E-5	0.122E-1	2199
0.59×10^{-2}	0.151E-3	0.497E-3	0.503E-5	0.764E-2	2130
0.156×10^{-1}	0.180E-3	0.131E-3	0.783E-5	0.251E-2	1957
0.216×10^{-1}	0.182E-3	0.643E-4	0.106E-4	0.217E-2	1869

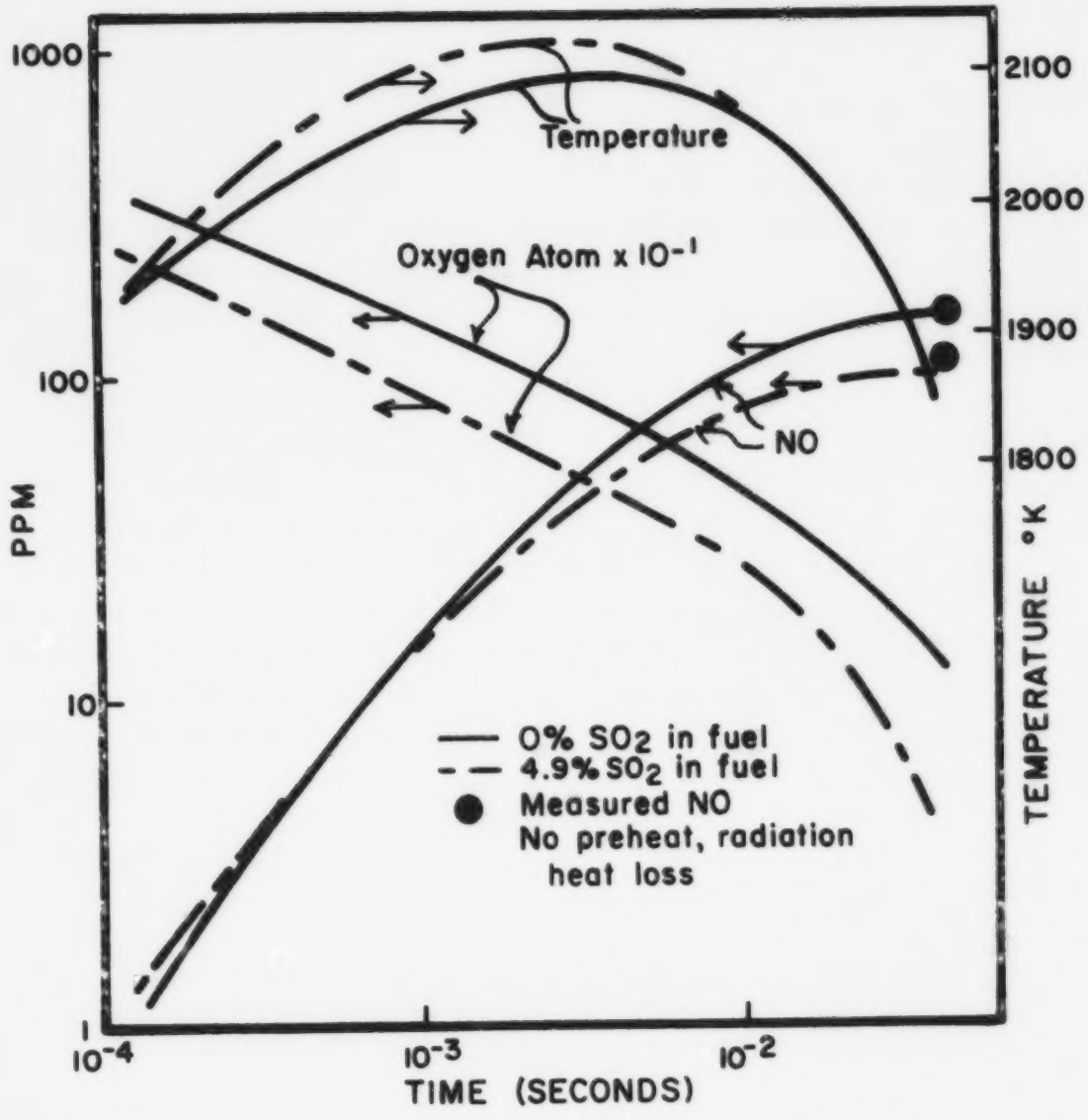

FIGURE 22. SO_2 ADDITION AFFECTS BOTH OXYGEN ATOM AND TEMPERATURE PROFILES, BUT LOWERS NO

It is instructive to examine the effect of SO_2 in the fuel on NO formation rates when there is zero radiative heat loss, i.e. under adiabatic conditions. This is shown in Figure 23 where it is apparent that under adiabatic conditions the presence of SO_2 causes NO to reach its equilibrium value more slowly. This simulation also indicated that SO_2 causes a change in the time temperature history, but that the primary effect was due to lower O atom concentrations.

In order to separate out kinetic and temperature effects it is useful to determine the role of SO_2 under a specified time-temperature history. In this case there is no attempt made to satisfy the heat balance, but rather it is assumed that the temperature and heat transfer are controlled by the furnace configuration. A realistic temperature history is one with an exponential temperature drop from 2100°K to 1050°K in one second. This time-temperature history is roughly representative of that felt by a labeled volume of premixed gas and fuel as it combusts and moves through the convection section of a furnace. Thus this simulation can give some indication of what might happen in a utility boiler, under conditions where fuel and air mixing is very rapid. Results are shown on Table 9, and indicate that under such conditions fuel sulfur is likely to inhibit the formation of NO_x.

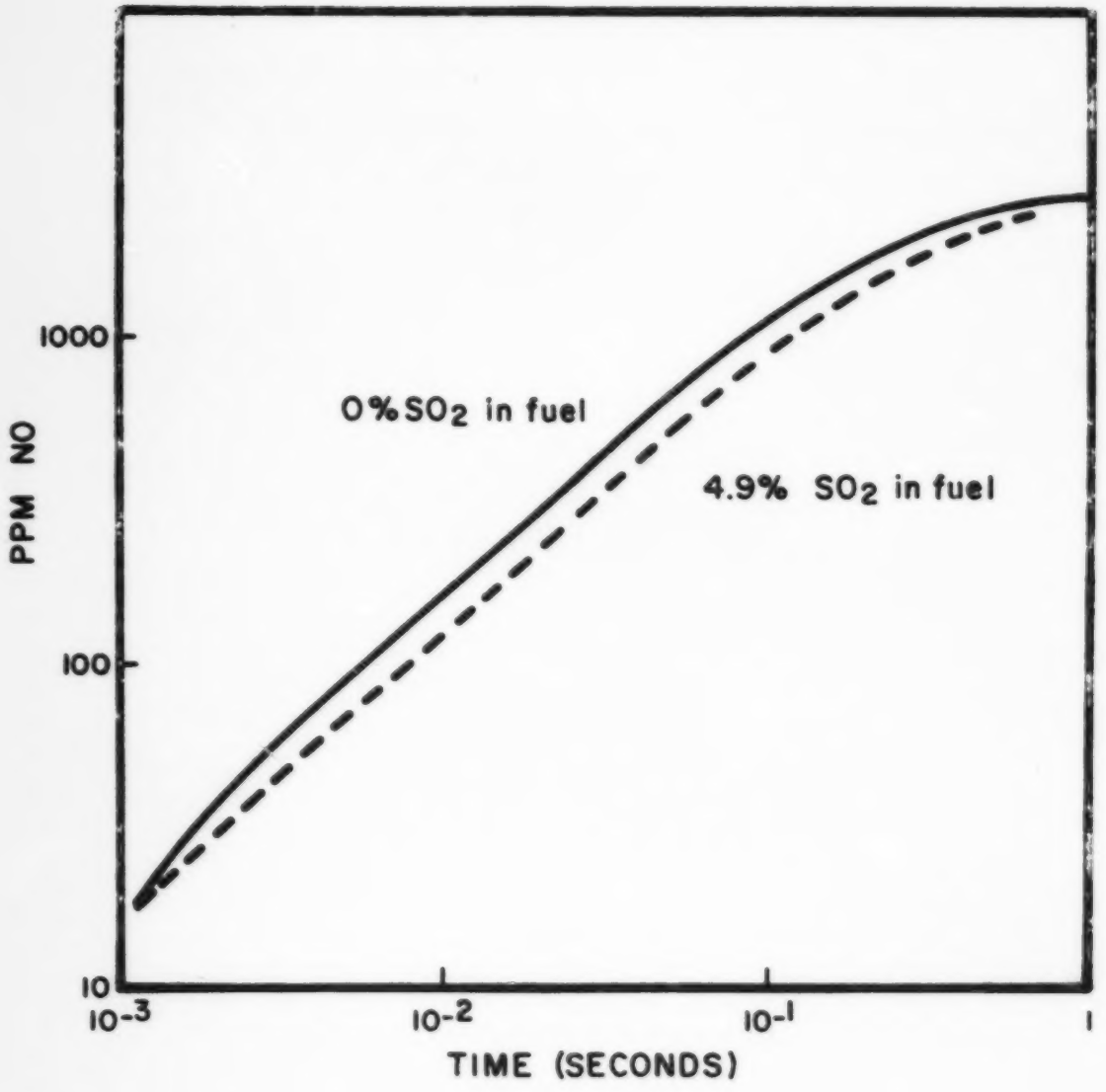

FIGURE 23. UNDER ADIABATIC CONDITIONS SO_2 DELAYS NO FORMATION

Table 9. FURNACE SIMULATION PREMIXED MIXTURE, SPECIFIED TEMPERATURE FALLING FROM 2100°K to 1050°K IN ONE SECOND. APPROXIMATELY 4% EXCESS AIR

	NO ppm	
Approximate Time	Without sulfur	With sulfur (4.9% SO_2 Fuel)
0.4 m sec	33.6	24.5
1 m sec	63.0	38.8
2.5 m sec	218.0	125.0
Exhaust	339.0	189.0

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PUBLICATIONS AND PRESENTATIONS RESULTING FROM GRANT R-802204

1) Wendt, J.O.L. and J.M. Ekmann, "Effect of Fuel Sulfur Species on Nitrogen Oxide Emissions from Premixed Flames" to be published in Combustion and Flame.

2) Wendt, J.O.L. and J.M. Ekmann, "Catalytic Inhibition of Nitrogen Oxide Formation by Sulfur Dioxide" presented at 67th Annual Meeting, AIChE, Washington, D.C., December 1974.

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4) Wendt, J.O.L. and J.M. Ekmann, "Effect of Fuel Sulfur on Nitrogen Oxide Emission" presented at EPA Stationary Source Combustion Symposium, Atlanta, Ga., September 24-26 1975. Proceedings to be published.

APPENDICES

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APPENDIX A. DESCRIPTION OF COMPUTER PROGRAM REKINET FOR INTEGRATING STIFF DIFFERENTIAL EQUATIONS ARISING IN KINETICS PROBLEMS

SUMMARY

A computer program, REKINET, for integrating sets of differential equations arising from kinetics problems is described. This program, which uses "a cantilevered implicit method" is especially suitable for systems of "stiff" equations such as result from problems with great disparity in characteristic reaction times, as for example, in combustion problems. Use of free format and internal tables of thermochemical and rate constant data make the program especially easy to use. Either well mixed stages or plug flow reactors or combinations of these types can be simulated with specified temperature histories or under heat balanced conditions. The integration method, TYSON, can be used independently of the chemical reaction features for difficult-to-integrate problems.

PURPOSE AND SCOPE

Program REKINET integrates the conservation equations for individual chemical species for a stirred-tank or plug-flow reactor. Temperature and pressure may be specified as functions of residence time in the reactor or a heat-balanced solution may be obtained. Up to 35 species may be handled. The reactions (up to 70 in number) may be unimolecular, biomolecular or thermolecular provided they can be represented by

$$A + B + C = D + E + F$$

where A, B, C, D, E, F represents a molecule or molecular fragment. One or two of the reactants or products can be missing. If a species is mentioned on both sides of the = sign it is taken to represent a non-reacting third body. The species name "M" represents a generalized third body. The program treats all species as ideal gases; however, liquid phase reactions can be

can be simulated by use of a (large) effective pressure.

The method integration used is based on the paper "An Implicit Integration Procedure for Chemical Kinetics", by T.J. Tyson and J.R. Kliegel, Paper No. 68-180, AIAA 6th Aerospace Sciences Meeting, (1968). This method of integration, which we call a "cantilevered implicit method" is especially suited to the integration of "stiff" equations such as arise when some of the species react very much faster than some other species as, for example, in combustion. No special precautions need be taken when formulating the equations to eliminate nearly equilibrated reactions as must be done, for example, when using explicit (predictor-corrector or Runge Kutta) methods. For reaction systems which are not "stiff" the program described is somewhat slower than explicit methods but it will often be found useful because of its convenient input and its general reliability. Since it is an implicit method, the program must calculate the partial derivatives of the rate expressions with respect to temperatures and the concentrations. This is done "analytically" under the assumption that the reactions are of integral order as implied by the way in which they are written and that the reaction rates can be calculated from

$$r_f = a_f \, T^{nf} \exp\left[-E_f/RT\right] C_a \, C_b \, C_c$$

$$r_r = a_r \, T^{nr} \exp\left[-E_r/RT\right] C_d \, C_e \, C_f$$

If less than three reactants or products are involved, the corresponding concentration in these equations are replaced by unity.

OUTPUT GENERATED

After printing out the input data the program calculates, prints

the temperature, pressure, gas density and species mole fractions as a function of residence time. A time step of variable size is used in the integration to reduce calculation time. The program also prints out the forward and reverse rates for each of the reactions considered at a number of time steps. This permits one to readily assess the importance of particular reactions and to determine which reactions are at equilibrium.

SAMPLE PROBLEM

A sample problem has been supplied to EPA. This problem is the base case simulation of the flat flame with the results shown in Table 7.

PROBLEM SETUP

The user will go through five phases in setting up a problem to be run on REKINET. First he must specify the type and size of reactor, whether plug flow, series of well mixed stages, or a well mixed stage followed by a plug flow reactor. Second, he must specify the kinetic mechanism, components and reactions with their rate constants. Third, he must specify amount and type of output. Fourth, he may wish to alter the normal accuracy criterion and other integration control parameters. The last phase is program execution.

This program uses a "free-format with control word" type of data card. Columns 1-6 of each card contain a control word (for example: VOLUME, EXECUT....) which functions as a machine instruction, directing the setting of a set of data or the use of a particular option. Card order in the data deck is immaterial (with certain minor and obvious exception, e.g., the EXECUT card is the last in each data deck). Below we describe briefly the function of each type of data card under the five phases of data preparation. Precise examples of the format of each type of card are given in Appendix II in which a sample data deck is exhibited.

Phase I. Reactor Configuration and Size

WELLSTIRRED	Calls for a well stirred reactor calculation
PLUGFLOW	Calls for a plug flow reactor following the well stirred stages
VOLUME	Determines the reciprocal space velocity) of the well stirred stage
TIMEIN AND TIMOUT	Sets the range of the independent variable (time or reciprocal space velocity) for the plug flow reactor
FLAMEM	Selects option to allow volume to be adjusted so that a given fraction X of a species designated "fuel" is converted, e.g., the card "FLAMEM, CH_4, 0.02....." designates that the volume of the well stirred stage should be such that the flow of CH_4 out is equal to 2% of the flow of CH_4 into the stage.
FDTEMP	Designates feed temperature, i.e., "FDTEMP, 298.0,..."
TEMPST	Designates first guess at outlet temperature for WSS
DILUEN	Specifies that an unnamed diluent is present
HTLOSS	Determines the factors governing heat loss
HEATBALANCE	Selects a heat balanced case as contrasted with specified temperature and pressure
PDECAY	Sets the pressure or pressure-time profile
TDECAY	Sets the temperature-time profile

Phase II. Defines the Reacting System in Terms of Species and Reactions

SPECIE	Defines a chemical species and sets its mole fraction in the feed and estimate of mole

fraction in product

ENTHAL	Feeds in heat of formation, and specific heat data
STOICH	Defines an elementary chemical reaction
FRATCO	Feeds in Arrhenius rate parameters for the forward direction of a reaction
RRATCO	Feeds in Arrhenius rate parameters for the reverse direction of a reaction

For certain species and reactions the THERMO cards are not needed. Internally stored data will be used. A reaction rate library supplies STOICH, FRATCO, and RRATCO cards for a large number of reactions.

Phase III. Output Control

NPRINT	Determines the frequency of detailed output for plug flow options. Suggested value 10.
PPRINT	Determines the frequency of detailed output for plug flow options.
TYDBUG	Determines degree of debug printout called for. For normal printout omit this card.
LEVEL	Determines extent of printout at each iteration.
RITEDATA	Determines whether diagnostic printout of free format interpreting routines is desired.

Phase IV. Integration Control

If not placed in the data deck, standard values for these parameters will be used.

SSCONT	Sets a parameter controlling step size
STEPIN	Gives an initial step size. If a value greater than 1000.0 is given the program calculates step size automatically.

MAXIT	Gives the maximum allowed number of iterations
WTFACT	Gives weighting factor for integration of the heat balanced WSS reactor.
VOLWTF	Gives weighting factor for the case where reactor volume is adjusted.

Phase V. The Execute Card

EXECUT	Turns control over to the machine to solve the problem and prints out the answer.

General Comments on Data Cards -

- Columns 1-6 are ordinarily for an indentifier word"*****, TYDBUG, SSCONT, STEPIN, TIMEIN, TIMOUT, TDECAY, PDECAY, FRATCO, RRATCO, STOICH, SPECIE, FLAMEM, PLUGFL, WELLST, VOLUME, NPRINT, PPRINT, LEVEL, WTFACT, VOLWTF, ENTHAL, MAXIT, HEATBA, or EXECUT"
- The card is punched free format with fields delimited by commas (or in the case of STOICH cards by + and = also). Blanks are not significant. Decimal points need not be punched. Large (or small numbers) may be represented by a magnitude multiplied by a power of 10., e.g., 123.4E-7.
- Card order is not significant except for the following point. The EXECUT card must be the last in the deck for that run.
- Certain "default" variables are built into the program. If the user does not insert a card certain cards are "understood" to be present. The user should check the program listing for the default values used.
- Certain identifer cards will cancel out previously desired options - e.g., NOWELL stirred, NOPLUG flow, NOHEAT balance, NOFLAME. Thus for several runs using the same deck, the pertinent identifier word is applicable. Built in default values set all options to FALSE at the beginning of the program.

- The program has built-in libraries of thermochemical constants derived from JANAF tables. Data cards ENTHAL have precedence over the internally stored data.
- Species names are left adjusted using the first 6 characters only and filling in on the right with blanks if there are fewer than 6 characters. The program does this automatically.
- Reactions are written with, + and = signs to delimit fields; the = sign separates the reactants from the products. By convention M represents a general gaseous third body.

General Comments on Conversion to Other Computer Systems - REKINET is written for a CDC 6400 computer, although versions compatible with UNIVAC 1110 systems are available. Conversion to other computer systems require changes in ENCODE and DECODE statements in sub-programs DESTOIC and DECIP. The CDC computer system uses words consisting of 10 characters. Conversion to systems with words consisting of 6 characters is simple since no names used need be longer than 6 characters. Conversion to systems with 4 characters per word (such as IBM 360) will be more difficult. REKINET is documented internally within the program listing.

APPENDIX B. SAMPLE DATA DECK

A computer listing of a sample data deck is shown on the following pages. This sample problem was run and the complete listing of REKINET and the output produced was sent to EPA. The sample problem is that of simulating nitrogen oxide formation from a flat flame.

```
SAMPLE PROBLEM INVOLVING FLAME MODEL AND PLUG FLOW HEAT BALANCED
**********************************************************************
***********
SIMULATION OF EKMANNS FLAT FLAME MAX NO CONDITION
**************
**********************************************************************
PLUGFLOW
HEATBALANCEDOPTION
WELLSTIRRED STAGE
VOLUME,1000.0,
VOLWTF,1.0,
FLAMEM,CH4,0.02,
SPECIE,CH4,0.1826E-02,0.0913,
SPECIE,O2,0.403E-01,0.1908,
SPECIE,N2,0.718,0.718,
SPECIE,CO,0.426E-01,
SPECIE,H2,0.139E-01,
SPECIE,O,0.4772E-02,
SPECIE,CHO,0.292E-04,
SPECIE,H,0.130E-01,
SPECIE,CO2,0.459E-01,
SPECIE,H2O,0.153E+00,
SPECIE,OH,0.816E-02,
SPECIE,HO2,0.977E-07,
SPECIE,N2O,0.916E-07,
SPECIE,CH2O,0.484E-03,
SPECIE,CH3,0.477E-03,
SPECIE,N,0.615E-09,
SPECIE,NO,0.499E-07,
PPRINT,5,
NPRINT,20,
FDTEMP,298.0,
TEMPST,1744.664,
ULTRASYSTEMS SET OF METHANE COMBUSTION KINETICS AFTER ADJUSTMENT
STOICH,ULT 36, CHO +M = CO + H + M,
FRATCO,ULT 36, 2.50E+20,-1.5,16.8,
RRATCO,ULT36, 3.23E+20,-1.5,-11.251,
STOICH,ULT77,CO2+M=CO+O+M,
FRATCO,ULT77,1.00E+15,0.,100.0,
RRATCO,ULT77,2.4785E+7,1.0,-27.7955,
STOICH,ULT84, H2O+M=OH+H+M,
FRATCO,ULT84,3.00E+15,0.0,105.0,
RRATCO,ULT84,15.756E+13,0.0,-14.628,
STOICH,ULT99,H+O+M=OH+M,
FRATCO,ULT99,8.00E+15,0.0,0.0,
RRATCO,ULT99,2.404E+21,-1.0,105.1481,
STOICH,ULT101,H+O2+M=HO2+M,
FRATCO,ULT101,1.50E+15,0.0,1.0,
RRATCO,ULT101,1.7573E+16,0.0,16.115,
STOICH,ULT140,N2O+M=N2+O+M,
FRATCO,ULT140,1.00E+14,0.0,50.0,
RRATCO,ULT140,2.351E+12,0.0,12.789,
STOICH,ULT44,CHO+H=CO+H2,
FRATCO,ULT44,3.00E+10,1.0,0.0,
```

```
RRATCO,ULT44,15.963E+10,1.0,76.3058,
STOICH,ULT46,CH2O+O=CHO+OH,
FRATCO,ULT46,2.0E+11,1.0,4.400,
RRATCO,ULT46,7.1865E+9,1.0,30.478,
STOICH,ULT47,CHO+OH=CO+H2O,
FRATCO,ULT47,3.00E+10,1.0,0.0,
RRATCO,ULT47,7.3837E+11,1.0,91.577,
STOICH,ULT52,CHO+O=CO+OH,
FRATCO,ULT52,3.00E+11,1.0,0.5,
RRATCO,ULT52,7.126E+11,1.0,74.895,
STOICH,ULT59,CH3+O=CH2O+H,
FRATCO,ULT59,2.00E+12,0.5,-0.3,
RRATCO,ULT59,2.497E+13,0.5,66.711,
STOICH,ULT63,CH4+O=CH3+OH,
FRATCO,ULT63,1.00E+10, 1.0,8.0,
RRATCO,ULT63,1.634E+8, 1.0,8.0,
STOICH,ULT65,CH4+H=CH3+H2,
FRATCO,ULT65,5.00E+10,1.0,10.0,
RRATCO,ULT65,18.783E+8,1.0,12.046,
STOICH,ULT66,CH4+OH=CH3+H2O,
FRATCO,ULT66,3.00E+13,0.,5.0,
RRATCO,ULT66,5.08E+12,0.0,22.182,
STOICH,ULT70,CO+OH=CO2+H,
FRATCO,ULT70,5.60E+11,0.0,1.080,
RRATCO,ULT70,7.32E+13,0.0,23.423,
STOICH,ULT83,H+OH=H2+O,
FRATCO,ULT83,8.00E+09,1.0,7.0,
RRATCO,ULT83,18.39E+9,1.0,9.046,
STOICH,ULT85,H+HO2=OH+OH,
FRATCO,ULT85,2.50E+14,0.0,1.9,
RRATCO,ULT85,23.43E+12,0.0,58.607,
STOICH,ULT88,OH+H2=H+H2O,
FRATCO,ULT88,2.50E+13,0.0,5.200,
RRATCO,ULT88,11.27E+13,0.0,20.336,
STOICH,ULT91,OH+N=H+NO,
FRATCO,ULT91,6.00E+11,0.5,8.0,
RRATCO,ULT91,16.794E+11,0.5,56.104,
STOICH,ULT98,H+N2O=OH+N2,
FRATCO,ULT98,8.00E+13,0.0,15.00,
RRATCO,ULT98,35.557E+11,0.0,80.235,
STOICH,ULT100, OH+O=H+O2,
FRATCO,ULT100,2.50E+13,0.0,0.0,
RRATCO,ULT100,3.303E+14,0.0,16.067,
STOICH,ULT117,OH+OH=H2O+O,
FRATCO,ULT117,6.00E+12,0.0,1.00,
RRATCO,ULT117,6.218E+13,0.0,18.182,
STOICH,ULT125,N+NO=N2+O,
FRATCO,ULT125,6.31E+11,0.5,0.0,
RRATCO,ULT125,28.105E+11,0.5,75.190,
STOICH,ULT133,N+O2=NO+O,
FRATCO,ULT133,6.00E+09,1.0,6.300,
RRATCO,ULT133,12.51E+8,1.0,38.198,
STOICH,ULT135,N2O+O=NO+NO,
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FRATCO,ULT135,1.00E+14,0.,28.0,
RRATCO,ULT135,0.02579E+14,0.0,66.011,
STOICH,ULT143,CHO+O2=CO+HO2,
FRATCC,ULT143,8.00E+12,0.0,0.0,
RRATCO,ULT143,15.34E+12,0.0,18.720,
ULTRASYSTEMS METHANE REACTION SET  WITHOUT CYANIDE ETC END
STOICH,   JOHN11,   O2+M=O+O+M,
FRATCO,   JOHN11,   51.19E18,          -1.0,   118.7,
RRATCO,   JOHN11,   25.63E17,          -1.0,   0.340,
ENTHAL,   CHO,-.2900E+01  , .979512E+00, .109102E+01,
                            .343380E-02,-.790833E-06,
ENTHAL,  CH2O,-.2770E+02  ,-.112187E+02, .311974E+01,
                            .582149E-02,-.147996E-05,
TIMOUT,0.1,
HTLOSS,3.45E-14,0.0,298.0,
EXECUTE
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APPENDIX C. REACTION RATE LIBRARY

The following pages show a computer listing of the reaction rate library which can be used with program REKINET. The reaction names are mnemonics derived from literature sources. Thus names LDSA, LDSB, LDSC etc. denote reactions from the Leeds University Reports Numbered 1, 2, 3 respectively. A complete bibliography of the reaction rate coefficient literature used in compiling this library can be found elsewhere (Sternling and Wendt, 1972). A copy of the reaction rate library, in punched computer card form has been sent to EPA.

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LISTING OF REACTION RATE LIBRARY  J. L. WENDT  JULY 10, 1973.
STOICH,   ARCUL1,   NO2   +SO2   =NO   +SO3,
FRATCO,   ARCUL1,   6.31E+12,          0.,   27.0,
RRATCO,   ARCUL1,   3A.24E+12,         0.,   35.980,
STOICH,   BROK1,   OH+H2=H2O+H,
FRATCO,   BROK1,   2.3E13,          0.0,   5.2,
STOICH,   BROK2,   H+O2=OH+O,
FRATCO,   BROK2,   2.04E4,          0.0,   16.50,
STOICH,   BROK3,   O+H2=OH+H,
FRATCO,   BROK3,   4.0E13,          0.0,   10.2,
STOICH,    BROK4,   H+O2+M=HO2+M,
FRATCO,   BROK4,   1.0E15,          0.0,   -1.3,
RRATCO,BROK4,   1.483E+15,   0.0,   45.471,
EQUILK,BROK4,  0.6741,   0.0,   -46.771,          PAGE 79
STOICH,   BROK4A,   H+O2+H2O=HO2+H2O,
FRATCO,   BROK4A,   30.0E+15,   0.0,   -1.3,
RRATCO,   BROK4A,   4.4503E+16,   0.0,   45.471,
EQUILK,BROK4A,   0.6741,   0.0,   -46.771,       PAGE 79
STOICH,   BROK5,   CO+OH=CO2+H,
FRATCO,   BROK5,   6.6E11,          0.0,   1.03,
STOICH,   BROK6,   H+HO2=OH+OH,
FRATCO,   BROK6,   7.0E13,          0.0,   0.0,
RRATCO,   BROK6,   0.6623E13,          0.0,   39.62,
STOICH,   BROK7,   OH+HO2=H2O+C2,
FRATCO,   BROK7,   6.0E12,          0.0,   0.0,
RRATCO,   BROK7,   7.702E+13,   0.0,   72.857,
EQUILK,   BROK7,   0.7790E-01,   0.0,   -72.857,   PAGE 57
STOICH,   BROK8,   O+HO2=OH+O2,
FRATCO,   BROK8,   6.0E12,          0.0,   0.0,
STOICH,   BROK9,   O+H2O=OH+OH,
FRATCO,   BROK9,   8.4E13,          0.0,   18.0,
STOICH,   BROK10,   H+HO2=H2+O2,
FRATCO,   BROK10,   2.3E13,          0.0,   0.0,
STOICH,   BROK11,   HO2+H2=HOOH+H,
FRATCO,   BROK11,   1.66E1,          0.0,   25.0,
STOICH,   BROK12,   HOOH+M=OH+OH+M,
FRATCO,   BROK12,   3.19E17,          0.0,   47.0,
STOICH,   BROK13,   HO2+HO2=HOOH+O2,
FRATCO,   BROK13,   1.8E12,          0.0,   0.0,
STOICH,   BROK14,   H+HOOH=H2O+OH,
FRATCO,   BROK14,   4.16E14,          0.0,   9.00,
STOICH,   BROK15,   O+HOOH=OH+HO2,
FRATCO,   BROK15,   9.0E13,          0.0,   1.00,
STOICH,   BROK16,   OH+HOOH=H2O+HO2,
FRATCO,   BROK16,   3.6E12,          0.0,   0.0,
STOICH,   BROK17,   CO+O2=CO2+O,
FRATCO,   BROK17,   2.5E12,          0.0,   48.0,
STOICH,   BROK18,   H2+M=H+H+M,
FRATCO,   BROK18,   1.12E13,          0.5,   92.6,
STOICH,   BROK19,   H+OH+M=H2O+M,
FRATCO,   BROK19,   1.0E19,          -1.0,   0.0,
STOICH,   BROK20,   O+O+M=O2+M,
FRATCO,   BROK20,   8.15E18,          -1.22,   0.0,
STOICH,   BROK21,   NO+HO2=NO2+OH,
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FRATCO,   BROK21,   1.0E13,          0.0,   0.0,
STOICH,   BROK22,   NO2+H=NO+OH,
FRATCO,   BROK22,   7.2E14,          0.0,   1.93,
STOICH,   BROK23,   O+NO2=NO+O2,
FRATCO,   BROK23,   1.9E13,          0.0,   1.06,
STOICH,   BROK24,   H+NO+M=HNO+M,
FRATCO,   BROK24,   4.0E15,   0.0,     -0.60,
STOICH,   BROK25,   H+HNO=H2+NO,
FRATCO,   BROK25,   5.0E13,          0.0,   0.0,
STOICH,   BROK26,   OH+HNO=H2O+NO,
FRATCO,   BROK26,   3.6E13,          0.0,   0.0,
STOICH,   BROK27,   O+HNO=CH+NO,
FRATCO,   BROK27,   3.0E13,          0.0,   0.0,
STOICH,   BROK28,   HO2+NO=HNO+O2,
FRATCO,   BROK28,   1.0E13,          0.0,   0.0,
STOICH,   BROK29,   O+NO+M=NO2+M,
FRATCO,   BROK29,   9.4E14,          0.0,   -1.93,
STOICH,   CBOW1,    H2   +   O2   =   OH   +   OH,
FRATCO,   CBOW1,    2.5E12,          0.0,   19.65,
STOICH,   CBOW2,    H   +   O2   =   OH   + O,
FRATCO,   CBOW2,    2.2E14,          0.0,   8.45,
STOICH,   CBOW3,    O   +   H2   =   OH   +   H,
FRATCO,   CBOW3,    1.7E13,          0.0,   4.76,
STOICH,   CBOW4,    H   +   H2O   =   H2   +   OH,
FRATCO,   CBOW4,    9.4E13,          0.0,   10.1,
STOICH,   CBOW5,    O   +   H2O   =   OH   +   OH,
FRATCO,   CBOW5,    5.8E13,          0.0,   9.07,
STOICH,   CBOW6,    H   +   H   +   ARGON=   H2   +   ARGON,
FRATCO,   CBOW6,    1.0E18,          -1.0,   0.0,
STOICH,   CBOW7,    H   +   H   +   N2=   H2   +   N2,
FRATCO,   CBOW7,    1.5E18,          -1.0,   0.0,
STOICH,   CBOW8,    O   +   O   +   ARGON=   O2   +   ARGON,
FRATCO,   CBOW8,    3.0E17,          -1.0,   0.0,
STOICH,   CBOW9,    O   +   O   +   N2=   O2   +   N2,
FRATCO,   CBOW9,    4.0E17,          -1.0,   0.0,
STOICH,   CBOW10,   H   +   OH   +   ARGON=   H2O   + ARGON,
FRATCO,   CBOW10,   0.20E20,          -1.0,   0.0,
STOICH,   CBOW11,   H   +   OH   +   N2   =   H2O
FRATCO,   CBOW11,   0.40E20,          -1.0,   0.0,
STOICH,   CBOW12,   H   +   OH   +   H2O   =   H2   +   H2O,
FRATCO,   CBOW12,   4.0E20,          -1.0,   0.0,
STOICH,   CBOW13,   H   +   O2   +   ARGON   =   HO2   +   ARGON,
FRATCO,   CBOW13,   1.6E15,          0.0,   0.504,
STOICH,   CBOW14,   H   +   O2   +   N2   =   HO2   +   N2,
FRATCO,   CBOW14,   3.0E15,          0.0,   0.504,
STOICH,   DAVI1,   O   +   HCN   =   NCO   +   H,
FRATCO,   DAVI1,   5.2E12,          0.0,   8.1,
STOICH,   DAVI2,   O   + CLCN   =   NCO   +   CL,
FRATCO,   DAVI2,   1.5E12,          0.0,   6.9,
STOICH,   DAVI3,   O   +   BRCN   =   NCO   +   BR,
FRATCO,   DAVI3,   1.4E13,          0.0,   9.7,
STOICH,   FENJ3,   N2O   + O=   NO   +   NO,
FRATCO,   FENJ3,   1.02E14,          0.0,   28.0,
STOICH,   GUTM1,   N2O   +   ARGON=   N2   +   O   +   ARGON,
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FRATCO,   GUTM1,      ,              -6.59,   60.0,
STOICH,   GUTM2,   N2O    + O    =N2    + O2,
FRATCO,   GUTM2,   0.85E14,            0.0,   28.0,
STOICH,   HOMER1,   H+    OH+    H2O=    H2O+    H2O
FRATCO,   HOMER1,   1.5E+25,          -2.6,    0.
RRATCO,   HOMER1,   28.43E+25,          -2.6,    119.63,
STOICH,   HOMER2,   H+    OH+    M=    H2O+    M
FRATCO,   HOMER2,   7.5E+23,          -2.6,    0.
RRATCO,   HOMER2,   1.4215E+25,          -2.6,    119.63,
STOICH,   JENKI1,   H    +SO2    +M    =HSO2    +M
FRATCO,   JENKI1,   7.256E+16,          0.0,    0.0
RRATCO,   JENKI1,   7.990E+16,          0.0,    46.3,
STOICH,   JENKI2,   HSO2    +OH    =H2O    +SO2
FRATCO,   JENKI2,   0.6789E+14,          0.0,    1.760
RRATCO,   JENKI2,   0.1169E+16,          0.0,    75.09
STOICH,   JOHN1,   O2+O2=O+O+O2,
FRATCO,   JOHN1,   27.52E18,          -1.0,    118.7,
RRATCO,   JOHN1,   13.78E17,          -1.0,    0.340,
STOICH,   JOHN2,   O2+ARGON=O+O+ARGON,
FRATCO,   JOHN2,   2.548E18,          -1.0,    118.7,
RRATCO,   JOHN2,   1.276E17,          -1.0,    0.340,
STOICH,   JOHN3,   O3+O3=O+O2+O3,
FRATCO,   JOHN3,   9.938E14,          0.0,    22.72,
RRATCO,   JOHN3,   16.79E12,          0.0,    -2.10,
STOICH,   JOHN4,   O+O3=O2+O2,
FRATCO,   JOHN4,   12.046E12,          0.0,    4.79,
RRATCO,   JOHN4,   12.77E12,          0.0,    100.6,
STOICH,   JOHN5,   O3+O2=O+O2+O2,
FRATCO,   JOHN5,   4.373E14,          0.0,    22.72,
RRATCO,   JOHN5,   7.388E12,          0.0,    -2.10,
STOICH,   JOHN6,   O3+HE=O+O2+HE,
FRATCO,   JOHN6,   3.379E14,          0.0,    22.72,
RRATCO,   JOHN6,   5.709E12,          0.0,    -2.10,
STOICH,   JOHN7,   O3+ARGON=O+O2+ARGON,
FRATCO,   JOHN7,   2.485E14,          0.0,    22.72,
RRATCO,   JOHN7,   4.198E12,          0.0,    -2.10,
STOICH,   JOHN8,   O3+N2=O+O2+N2,
FRATCO,   JOHN8,   3.876E14,          0.0,    22.72,
RRATCO,   JOHN8,   6.548E12,          0.0,    -2.10,
STOICH,   JOHN9,   O3+CO2=O+O2+CO2,
FRATCO,   JOHN9,   9.540E14,          0.0,    22.72,
RRATCO,   JOHN9,   16.12E12,          0.0,    -2.10,
STOICH,   JOHN10,   O3+H2O=O+O2+H2O,
FRATCO,   JOHN10,   38.16E14,          0.0,    22.72,
RRATCO,   JOHN10,   64.48E12,          0.0,    -2.10,
STOICH,   JOHN11,   O2+M=O+O+M,
FRATCO,   JOHN11,   51.19E18,          -1.0,    118.7,
RRATCO,   JOHN11,   25.63E17,          -1.0,    0.340,
STOICH,   JOHN12,   O3+M=O+O2+M,
FRATCO,   JOHN12,   7.233E14,          0.0,    22.72,
RRATCO,   JOHN12,   12.22E12,          0.0,    -2.10,
STOICH,   LANG1,   N2 + O= NO + N,
FRATCO,   LANG1,   6.68E13,          0.0,    75.230,
RRATCO,   LANG1,   1.0E13,          0.0,    0.0,
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STOICH,   LANG2,   N2 + HO2 = NO+ HNO,
FRATCO,   LANG2,   7.9E10,          0.5,   41.8,
RRATCO,   LANG2,   9.59E11,         0.0,   2.501,
STOICH,   LANG3,   N2 + O + M = N2O + M,
FRATCO,   LANG3,   1.62E11,         0.0,   3.180,
RRATCO,   LANG3,   7.25E12,         0.0,   40.7,
STOICH,   LANG4,   N2 + OH = N2O + H,
FRATCO,   LANG4,   1.18E12,         0.0,   75.8,
RRATCO,   LANG4,   3.0E13,          0.0,   10.77,
STOICH,   LANG5,   N2 + O2 = N2O + O,
FRATCO,   LANG5,   2.88E14,         0.0,   107.8,
RRATCO,   LANG5,   5.3E14,          0.0,   26.7,
STOICH,   LANG6,   N2 + NO2 = N2O + NO,
FRATCO,   LANG6,   4.5E14,     0.0, 84.3,
RRATCO,   LANG6,   2.5E14,          0.0,   50.0,
STOICH,   LANG7,   N + O2 = NO + O,
FRATCO,   LANG7,   1.41E13,         0.0,   7.9,
RRATCO,   LANG7,   2.95F12,         0.0,   39.9,
STOICH,   LANG8,   N + OH = NO + H,
FRATCO,   LANG8,   5.3E11,          0.5,   5.62,
RRATCO,   LANG8,   9.53F13,         0.0,   55.0,
STOICH,   LANG9,   N2O + O = NO + NO,
FRATCO,   LANG9,   6.3E14,          0.0,   26.7,
RRATCO,   LANG9,   1.61E13,         0.0,   64.5,
STOICH,   LANG10,   N2O + O2 = NO + NO2,
FRATCO,   LANG10,   6.0E14,         -1.5,   9.9,
RRATCO,   LANG10,   2.0E9,          0.0,   3.22,
STOICH,   LANG11,   N + OH = NH + O,
FRATCO,   LANG11,   1.29E14,          0.0,   18.0,
RRATCO,   LANG11,   1.0E12,         0.5,   0.1,
STOICH,   LANG12,   N + H2 = NH + H,
FRATCO,   LANG12,   1.32F15,          0.0,   22.3,
RRATCO,   LANG12,   1.0E12,         0.68,   1.9,
STOICH,   LANG13,   N + H2O = NH + OH,
FRATCO,   LANG13,   3.59E15,          0.0,   38.6,
RRATCO,   LANG13,   1.6E12,         0.56,   1.5,
STOICH,   LANG14,   NH + OH = NO + H2,
FRATCO,   LANG14,   1.6E12,         0.56,   1.5,
RRATCO,   LANG14,   2.22E15,          0.0,   69.6,
STOICH,   LANG15,   NH + O = NO + H,
FRATCO,   LANG15,   5.0E11,         0.5,   5.0,
RRATCO,   LANG15,   1.84E14,          0.0,   71.0,
STOICH,   LANG16,   NH + OH = HNO + H,
FRATCO,   LANG16,   6.44E11,          0.0,   2.9,
RRATCO,   LANG16,   2.0E11,         0.5,   13.0,
STOICH,   LANG17,   NH + O2 = HNO + O,
FRATCO,   LANG17,   4.38E12,          0.0,   13.0,
RRATCO,   LANG17,   1.0E11,         0.5,   7.0,
STOICH,   LANG18,   HNO + M = H + NO + M,
FRATCO,   LANG18,   1.9E16,         0.0,   50.0,
RRATCO,   LANG18,   3.1E15,         0.0,   0.7,
STOICH,   LANG19,   HNO + OH = NO + H2O,
FRATCO,   LANG19,   2.1E12,         0.5,   0.0,
RRATCO,   LANG19,   4.1E14,         0.5,   71.5,
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STOICH,   LANG20,   HNO + H = NO + H2,
FRATCO,   LANG20,   1.4E13,          0.0,   3.0,
RRATCO,   LANG20,   9.5E12,          0.0,   58.0,
STOICH,   LANG21,   HNO + O = NO + OH,
FRATCO,   LANG21,   5.0E11,          0.5,   0.0,
RRATCO,   LANG21,   9.3E12,          0.0,   54.5,
STOICH,   LOSA 1,   CO+   OH=   CO2+   H
FRATCO,   LOSA 1,   5.6E+11,          0.0,   1.080,
RRATCO,   LOSA 1,   7.29E+13,         0.0,   23.410,
STOICH,LOSB 1,      H2       +O       =H       +OH      ,
FRATCO,LOSB 1,      1.7  E+13,     0.00,9.45     ,
RRATCO,LOSB 1,  7.3E+12,  0.00,  7.3
STOICH,LOSB 3,      H2       +OH      =H2O     +H       ,
FRATCO,LOSB 3,      2.19 E+13,     0.00,5.15     ,
RRATCO,LOSB 3,      8.41 E+13,     0.00,20.1     ,
STOICH,LOSB 5,      H2O      +O       =OH      +OH      ,
FRATCO,LOSB 5,      5.75 E+13,     0.00,18.0     ,
RRATCO,LOSB 5,      5.75 E+12,     0.00,.78      ,
STOICH,LOSB 7,      H2O      +M       =H       +OH      +M       ,
FRATCO,LOSB 7,      3.4  E+05,     0.00,0.0      ,
RRATCO,LOSB 7,      1.17 E+17,     0.00,0.0      ,
STOICH,LOSC 1,      O2       +H       =O       +OH      ,
FRATCO,LOSC 1,      2.24 E+14,     0.00,16.8     ,
RRATCO,LOSC 1,      1.3  E+13,     0.00,0.00     ,
STOICH,LOSC 3,      O2       +H       +M       =HO2     +M       ,
FRATCO,LOSC 3,      1.59 E+15,     0.00,1.0      ,
RRATCO,LOSC 3,      2.4  E+15,     0.00,45.9     ,
STOICH,LOSC 5,      H2O2     +H       =H2      +HO2     ,
FRATCO,LOSC 5,      2.34 E+13,     0.00,9.2      ,
RRATCO,LOSC 5,      9.6  E+12,     0.00,24.0     ,
STOICH,LOSC 7,      H2O2     +H       =H2O     +OH      ,
FRATCO,LOSC 7,      3.18 E+14,     0.00,9.0      ,
RRATCO,LOSC 7,      5.6  E+13,     0.00,77.9     ,
STOICH,LOSC 9,      H2O2     +OH      =H2O     +HO2     ,
FRATCO,LOSC 9,      1.00 E+13,     0.00,1.8      ,
RRATCO,LOSC 9,      2.8  F+13,     0.00,32.7     ,
STOICH,LOSC11,      H2O2     +M       =OH      +OH      +M       ,
FRATCO,LOSC11,      1.17 E+17,     0.00,45.5     ,
RRATCO,LOSC11,      8.4  E+14,     0.00,5.3      ,
STOICH,LOSD 1,      NO       +N       =N2      +O       ,
FRATCO,LOSD 1,      3.10 E+13,     0.00,.334     ,
RRATCO,LOSD 1,      1.36 E+14,     0.00,75.4     ,
STOICH,LOSD 3,      O2       +N       =NO      +O       ,
FRATCO,LOSD 3,      6.43 E+09,     1.00,6.25     ,
RRATCO,LOSD 3,      1.55 E+09,     1.00,38.64    ,
STOICH,LOSD 5,      N        +O       +M       =NO      +M       ,
FRATCO,LOSD 5,      3.9  E+15,     0.00,*********,
RRATCO,LOSD 5,      *****E+**,     0.00,*********,
STOICH,LOSD 7,      N2       +O2      =NO      +NO      ,
FRATCO,LOSD 7,      *****E+**,     0.00,*********,
RRATCO,LOSD 7,      *****E+**,     0.00,*********,
STOICH,LOSD 9,      N2O      +O       =NO      +NO      ,
FRATCO,LOSD 9,      6.0  E+14,     0.00,26.7     ,
RRATCO,LOSD 9,      1.0  F+14,     0.00,76.0     ,
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STOICH,LOSD11,      NO2       +M          =NO         +NO         ,
FRATCO,LOSD11,      1.1   E+13,       0.00,0.0       ,
RRATCO,LOSD11,      1.0   E+10,       0.00,88.0      ,
STOICH,LOSE 1,      NO2       +O          =NO         +O2         ,
FRATCO,LOSE 1,      1.0   E+13,       0.00,.6        ,
RRATCO,LOSE 1,      1.0   E+12,       0.00,45.5      ,
STOICH,LOSE 3,      NO2       +M          =NO         +O          +M          ,
FRATCO,LOSE 3,      1.1   E+16,       0.00,65.0      ,
RRATCO,LOSE 3,      1.05  E+15,       0.00,1.87      ,
STOICH,LOSE 5,      NO        +C          =NO2        +HV         ,
FRATCO,LOSE 5,      *****E+**,        0.00,**********,
STOICH,LOSE 6,      NO        +NO         +O2         =NO2        +NO2        ,
FRATCO,LOSE 6,      2.4   E+09,       0.00,-1.05     ,
RRATCO,LOSE 6,      4.0   E+12,       0.00,26.9      ,
STOICH,    MERL1,   SO2   + O   +   M   = SO3   + M,
FRATCO,    MERL1,   2.4E17,            0.0,   2.50,
RRATCO,    MERL1 ,  11.538E+19,              0.0,   83.090,
STOICH,    MERL3A,  SO3   +   O   = SO2   +   O2,
FRATCO,    MERL3A,  2.8E14,            0.0,   12.0,
RRATCO,    MERL3A,  14.18E+12,               0.0,   49.930,
STOICH,    NEWH1,   H2O+M=OH+H+M,   SYMCA-1969-12-604
FRATCO,    NEWH1,   5.4E17,     0.0,123.6,
RRATCO,    NEWH1,   1.5E16,            0.0,   0.0,
STOICH,    NEWH2,   H2+M=H+H+M,     SYMCA-1969-12-604,
FRATCO,    NEWH2,   3.1E15,            0.0,   110.0,
RRATCO,    NEWH2,   7.0E17,            -1.0,  0.0,
STOICH,    NEWH3,   NO+M=N+O+M,     SYMCA-1969-12-604,
FRATCO,    NEWH3,   3.989E20,               -2.5,  150.0,
RRATCO,    NEWH3,   0.9E15,            0.0,   0.0,
STOICH,    NEWH4,   N2+M=N+N+M,     SYMCA-1969-12-604,
FRATCO,    NEWH4,   4.754E17,               -1.5,  224.9,
RRATCO,    NEWH4,   6.1E14,            0.0,   0.0,
STOICH,    NEWH5,   N2O+M=N2+O+M,   SYMCA-1969-12-604,
FRATCO,    NEWH5,   1.0E15,            0.0,   61.0,
RRATCO,    NEWH5,   1.82E13,           0.0,   21.4,
STOICH,    NEWH6,   NO2+M=NO+O+M,   SYMCA-1969-12-604,
FRATCO,    NEWH6,   5.4E21,            -1.0,  74.0,
RRATCO,    NEWH6,   2.0E16,            0.0,   0.0,
STOICH,    NEWH7,   O2+M=O+O+M,     SYMCA-1969-12-604,
FRATCO,    NEWH7,   3.563E19,               -1.0,  118.0,
RRATCO,    NEWH7,   1.0E14,            0.0,   0.0,
STOICH,    NEWH8,   OH+H=H2+O,      SYMCA-1969-12-604,
FRATCO,    NEWH8,   1.4E12,            0.0,   6.0,
RRATCO,    NEWH8,   3.3E12,            0.0,   8.00,
STOICH,NEWH9,       OH+O=O2+H,       SYMCA-1969-12-604,
FRATCO,    NEWH9,   5.5E13,            0.0,   1.0,
RRATCO,    NEWH9,   7.2E14,            0.0,   16.9,
STOICH,    NEWH10,   OH+H2=H2O+H,     SYMCA-1969-12-604,
FRATCO,    NEWH10,   6.2E13,           0.0,   6.0,
RRATCO,    NEWH10,   3.2E14,           0.0,   21.1,
STOICH,    NEWH11,   OH+OH=H2O+O,     SYMCA-1969-12-604,
FRATCO,    NEWH11,   7.7E12,           0.0,   1.00,
RRATCO,    NEWH11,   8.3E13,           0.0,   18.1,
STOICH,    NEWH12,   CO+OH=CO2+H,     SYMCA-1969-12-604,
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FRATCO,   NEWH12,   7.1E12,          0.0,   7.7,
RRATCO,   NEWH12,   4.7E14,          0.0,   27.25,
STOICH,   NEWH13,   NO+O=O2+N,    SYMCA-1969-12-604,
FRATCO,   NEWH13,   3.2E9,           1.0,   39.10,
RRATCO,   NEWH13,   13.3E9,          1.0,   7.08,
STOICH,   NEWH14,   NO+N=N2+O,    SYMCA-1969-12-604,
FRATCO,   NEWH14,   1.55E13,         0.0,   0.0,
RRATCO,   NEWH14,   7.0E13,          0.0,   75.50,
STOICH,   NEWH15,   NO+O2=NO2+O,  SYMCA-1969-12-604,
FRATCO,   NEWH15,   0.18E11,         0.5,   47.0,
RRATCO,   NEWH15,   0.58E11,         0.5,   0.0,
STOICH,   NEWH16,   NO+NO=N2O+O,  SYMCA-1969-12-604,
FRATCO,   NEWH16,   2.6E12,          0.0,   63.8,
RRATCO,   NEWH16,   1.42E14,         0.0,   28.0,
STOICH,   NEWH17,   H+O2+M=HO2+M,  SYMCA-1969-12-604,
FRATCO,   NEWH17,   1.3E15,          0.0,   0.0,
STOICH,   PATT1,   CN+CN=C2+N2,      JCPSA-1962-36-1146
FRATCO,    PATT1,   1.6E15,          0.0,   43.0
STOICH,   PATT1,   CN+CN=C2+N2,      JCPSA-1962-36-1146
FRATCO,    PATT1,   1.6E15,          0.0,   43.0
STOICH,   PYDY16,   NO   +O2   +M   =NO3   +M,
FRATCO,   PYDY16,   3.697E+08,          0.,   4.220,
RRATCO,   PYDY16,   2.26E+11,           0.,   4.420,
STOICH,   PYDY29,   NO3   +NO   =NO2   +NO2 ,
FRATCO,   PYDY29,   9.216E+11,          0.0,  -0.6,
RRATCO,   PYDY29,   3.9E+11,           0.,   23.9,
STOICH,SBOW 1,CH4+M=CH3+H+M ,
FRATCO,SBOW 1,1.5E+19,    0.,99.594,
RRATCO,SBOW 1,13.34E+16,     0.,-2.846,
STOICH,SBOW 2,CH4+C2=CH3+HO2,
FRATCO,SBOW 2,1.0E+14,     0.,44.946,
RRATCO,SBOW 2,1.32E+12,     0.,-10.724,
STOICH,SBOW 3,O2+M=O+O+M,
FRATCO,SBOW 3,3.6E+18,     -1.0,117.612,
RRATCO,SBOW 3,14.78E+16,    -1.0,-0.918,
STOICH,SBOW 4,CH4+O=CH3+OH,
FRATCO,SBOW 4,1.7E+13,    0.,8.672,
RRATCO,SBOW 4,2.8E+11,     0.,8.692,
STOICH,SBOW 5,CH4+H=CH3+H2,
FRATCO,SBOW 5,6.3E+13,     0.,12.573,
RRATCO,SBOW 5,23.56E+11,     0.,14.623,
STOICH,SBOW 6,CH4+OH=CH3+H2O,
FRATCO,SBOW 6,2.8E+13,     0.,4.950,
RRATCO,SBOW 6,4.72E+12,    0.,22.140,
STOICH,SBOW 7,CH3+O=HCHO+H,
FRATCO,SBOW 7,1.0E+14,     0.,0.,
RRATCO,SBOW 7,1.255E+15,     0.,67.020,
STOICH,SBOW 8,CH3+O2=HCHO+OH,
FRATCO,SBOW 8,1.0E+12,     0.,0.,
RRATCO,SBOW 8,9.55E+11,     0.,50.950,
STOICH,SBOW 9,HCHO+OH=CHO+H2O,
FRATCO,SBOW 9,1.0E+14,     0.,0.,
RRATCO,SBOW 9,3.69E+13,     0.,43.260,
STOICH,SBOW10,CHO+CH=CO+H2O,
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FRATCO,SBOW10,1.0E+14,     0.,0.,
RRATCO,SBOW10,2.45E+15,     0.,91.590,
STOICH,SBOW11,CO+OH=CO2+H,
FRATCO,SBOW11,3.1E+11,     0.,0.594,
RRATCO,SBOW11,4.04E+13,     0.,22.924,
STOICH,SBOW12,H+O2=O+OH,
FRATCO,SBOW12,2.2E+14,     0.,16.454,
RRATCO,SBOW12,0.167E+14,     0.,0.384,
STOICH,SBOW13,O+H2=H+OH,
FRATCO,SBOW13,4.0E+14,     0.,9.365,
RRATCO,SBOW13,1.762E+14,     0.,7.335,
STOICH,SBOW14,O+H2O=OH+OH  ,
FRATCO,SBOW14,8.4E+14,     0.,18.058,
RRATCO,SBOW14,0.820E+14,     0.,0.888,
STOICH,SBOW15,H+H2O=H2+OH,
FRATCO,SBOW15,1.0E+14,     0.,20.196,
RRATCO,SBOW15,0.22E+14,     0.,5.056,
STOICH,SBOW16,H+OH+M=H2O+M,
FRATCO,SBOW16,2.00E+19,     -1.0,0,
RRATCO,SBOW16,3.79E+20,     -1.0,119.630,
STOICH,SBOW18,CHO+M=H+CO+M,
FRATCO,SBOW18,2.0E+13,     0.5,28.512,
RRATCO,SBOW18,2.58E+13,     0.5,0.472,
STOICH,    SEMNO3,    NO3    +SO2    =SO3    +NO2,
FRATCO,    SEMNO3,    0.5325E+13,                0.0,    2.050,
RRATCO,    SEMNO3,    0.1365E+14,                0.0,    35.530,
STOICH,WILD 1,H2+NC=HNO+H,
FRATCO,WILD 1,1.4E+13,     0.0,54.9,
RRATCO,WILD 1,7.0E+13,     0.0,3.0,
STOICH,WILD 3,OH+H2=H2O+H,
FRATCO,WILD 3,3.9E+13,     0.0,5.49,
RRATCO,WILD 3,1.8E+14,     0.0,20.7,
STOICH,WILD 5,N2O+H=N2+OH,
FRATCO,WILD 5,3.0E+13,     0.0,10.77,
RRATCO,WILD 5,1.3E+13,     0.0,76.0,
STOICH,WILD 6,HNO+OH=NO+H2O,
FRATCO,WILD 6,2.0E+14,     0.0,3.0,
RRATCO,WILD 6,6.2E+14,     0.0,73.31,
STOICH,WILD 7,H+NO+M=HNO+M,
FRATCO,WILD 7,3.2E+19,     -1,0,00.0
RRATCO,WILD 7,1.0E+19,     -1.0,46.0,
STOICH,WILD 9,HNO+NO=N2O+OH,
FRATCO,WILD 9,2.0E+12,     0.0,26.0,
RRATCO,WILD 9,2.4E+13,     0.0,41.13,
STOICH,WILD10,HNO+HNO=N2O+H2O,
FRATCO,WILD10,3.0E+11,     0.0,3.5,
RRATCO,WILD10,1.1E+13,     0.0,88.94,
STOICH,WILD11,N2O+M=N2+O+M,
FRATCO,WILD11,5.0E+14,     0.0,58.0,
RRATCO,WILD11,1.2E+13,     0.0,20.77,
STOICH,WILD12,NO+NC=N2O+O,
FRATCO,WILD12,2.6E+12,     0.0,63.8,
RRATCO,WILD12,2.0E+14,     0.0,28.0,
STOICH,WILD13,O+H2=OH+H,
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FRATCO,WILD13,1.3E+13,     0.0,9.4,
RRATCO,WILD13,1.5E+11 ,     0.0,6.95,
STOICH,WILD14,H2O+O=OH+OH,
FRATCO,WILD14,9.2E+13,     0.0,18.0,
RRATCO,WILD14,7.6E+12,     0.0,1.0,
STOICH,WILD15,H2+M=H+H+M,
FRATCO,WILD15,4.2E+19,     -0.84,103.2,
RRATCO,WILD15,5.0E+18,     -1.0,0.0,
STOICH,WILD17,H+OH+M=H2O+M,
FRATCO,WILD17,1.8E+22,     -1.5,0.0,
RRATCO,WILD17,1.0E+24,     -1.34,118.0,
STOICH,WILD20,O+NO=N+O2,
FRATCO,WILD20,3.2E+09,     1.0,39.1,
RRATCO,WILD20,1.6E+10,     1.0,7.2,
STOICH,WILD22,N+NO=N2+O,
FRATCO,WILD22,1.5E+13,     0.0,0.0,
RRATCO,WILD22,6.9E+13,     0.0,75.25,
STOICH,WILD24,H+O2=OH+O,
FRATCO,WILD24,9.5E+13,     0.0,14.7,
RRATCO,WILD24,2.2E+12,     0.0,0.0,
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APPENDIX D. THERMOCHEMICAL LIBRARY

A listing of the thermochemical library can be found on the following pages. These data are presently stored internally in REKINET. A punched copy has been sent to EPA for their use. Each card has the following format:

ENTHAL, [name of species], [ΔH_f], [ACP], [BCP]

[CCP], [DCP].

where ΔH_f is the standard heat of formation of the species and the specific heat of the species, C_p, has the following dependence on temperature:

$$C_p = ACP + BCP \cdot \log_e T + CCP \cdot T + DCP \cdot T^2$$

The coefficients ACP, BCP, CCP and DCP were derived from a least squares fit through JANAF data. Errors of up to 8% in C_p are possible, as a result of this, although in general the errors are much smaller.

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------    THERMOCHEMICAL LIBRARY---------- OCT 2.1974  JOLN UNIV ARIZ
ENTHAL,    BR,..267403E+02 ..797545E+01 ,-.604109E+00..161075E-02 ,-.293159E-06,
ENTHAL,    BR2,..731703E+01 ..529175E+01 ..623262E+00 ,-.691404E-03,.124557E-06 ,
ENTHAL,    BRO,..300E+02     ,-.31E+01    ..19?E+01     ,-.19?E-02    ,.29?E-06    ,
ENTHAL,      C, .171946E+01,.470534E+01 ..569794E-01 ,-.199938E-03,.678161E-07 ,
ENTHAL,    CCL,.132030E+01 ,-.100499E+01,.161498E+01 ,-.159954E-02,.218320E-06 ,
ENTHAL, CCL2O,-.52400?E+02,-.210464E+02,..677234E+01 ,-.596611E-02,.738746E-06 ,
ENTHAL,   CCL4,-.229400E+02,-.629423E+02,..914174E+01 ,-.106525E-01,.157862E-05 ,
ENTHAL,   C2N2,.73?700E+02 ,-.110718E+02,..435479E+01 ,-.598851E-03,-.202231E-06,
ENTHAL,    CH2,..950000E+02 ,-.210465E+01,..169433E+01 ,.370539E-02 ,-.840596E-06,
ENTHAL,  CH2CL,.264E+02     ,-.275E+02    ,.671E+01     ,.393E-02     ,-.124E-05    ,
ENTHAL, CH2CL2,-.224300E+02,-.160581E+02,..856319E+01 ,-.226227E-02,-.120776E-05,
ENTHAL,    CH3,..319400E+02 ,-.449517E+01,..195038E+01 ,.705692E-02 ,-.160034E-05,
ENTHAL,  CH3CL,-.206600E+02,-.275510E+02,..631455E+01 ,.392855E-02 ,-.123865E-05,
ENTHAL,    CH4,-.179950E+02,-.949548E+01,..234033E+01 ,.119283E-01 ,-.260493E-05,
ENTHAL,   CH3O,..350E+01     ,..149E+02    ,.0.0         ,.0.0         ,.0.0         ,
ENTHAL, CH3O2,..679E+01     ,..160E+02    ,.0.0         ,.0.0         ,.0.0         ,
ENTHAL,CH3O2H,-.313E+02     ,..140E+02    ,.0.0         ,.0.0         ,.0.0         ,
ENTHAL,     CN,..111000E+03 ,.591157E+01 ,.247814E+00 ,.116999E-02 ,-.981735E-07,
ENTHAL,     CO,-.264170E+02,..740841E+01 ,-.288039E+00,.259841E-02 ,-.528510E-06,
ENTHAL,   COCL,-.150000E+02,-.144162E+01,..217928E+01 ,-.644645E-03,-.418559E-07,
ENTHAL,    CO2,-.940540E+02,-.147906E+02,..421328E+01 ,-.133161E-02,-.273210E-07,
ENTHAL,    COS,-.339400E+02,-.143695E+02,..419556E+01 ,-.262842E-02,..247469E-05 ,
ENTHAL,     C2,         0.0 ,-.289382E+02,..617905E+01 ,-.310483E-02,..314913E-06 ,
ENTHAL,     CS,..550000E+02 ,-.194768E+01,..162157E+01 ,-.809223E-03,-.379349E-07 ,
ENTHAL,    CS2,..279400E+02 ,-.133310E+02,..444771E+01 ,-.374760E-02,..447614E-06 ,
ENTHAL,     CL,..288270E+02 ,..629994E+00 ,..935357E+01 ,-.187911E-02,..331785E-05 ,
ENTHAL,    CL2,         0.0 ,..303149E+00 ,..146094E+01 ,-.171363E-02,..288674E-06 ,
ENTHAL,   CL2O,..210000E+02 ,-.846945E+01,..331204E+01 ,-.461269E-02,..688258E-06 ,
ENTHAL,    CLO,..241920E+02 ,-.313724E+01,..197288E+01 ,-.195125E-02,..293567E-06 ,
ENTHAL,   CLO2,..250000E+02 ,-.167319E+02,..432335E+01 ,-.453477E-02,..686019E-06 ,
ENTHAL,      H, .521000E+02,..446340E+01 , .788487E-03,-.150707E-05,..247103E-09 ,
ENTHAL,    HBR ,-.871300E+01,..110257E+02 ,-.887445E+00,..342143E-02 ,-.615252E-06,
ENTHAL,     HCL,-.220630E+02,..123366E+02 ,-.111960E+01,..355006E-02 ,-.599331E-06,
ENTHAL,     HCN,..312000E+02 ,-.431669E+01,..217006E+01 ,..195511E-02 ,-.456911E-06,
ENTHAL,     HCO,-.290000E+01,..979512E+00 ,..103192E+01 ,..341380E-02 ,-.798833E-06,
ENTHAL,  HCOCL,-.401E+02     ,..891E+01    ,.0.0         ,.0.0         ,.0.0         ,
ENTHAL,      H2,         0.0 ,..107652E+02 ,-.766202E+00,..194394E-02 ,-.163972E-06,
ENTHAL,     H2O,-.577940E+02,..144683E+02 ,-.145253E+01,..644539E-02 ,-.102179E-05,
ENTHAL,    H2O2,-.325130E+02,-.230056E+02,..609937E+01 ,-.525604E-02,..116404E-05 ,
ENTHAL,     H2S,-.484030E+01,..739354E+01 ,-.164465E+00,..576350E-02 ,-.113534E-05,
ENTHAL,   H2SO4,-.177000E+03,-.670409E+02,..157376E+02 ,-.112761E-01,..133546E-05 ,
ENTHAL,  H2SO4,,-.194544E+03,-.713213E+02,..197648E+02 ,-.281095E-01,..515231E-05 ,
ENTHAL,     HNO,..218000E+02 ,-.274905E+01,..179998E+01 ,..233806E-02 ,-.629637E-06,
ENTHAL,  HNO2,C,-.193430E+02,-.229669E+02,..694514E+01 ,-.234361E-02,..841345E-07 ,
ENTHAL,  HNO2,T,-.184400E+02,-.221725E+02,..694514E+01 ,-.248078E-02,..135233E-06 ,
ENTHAL,    HNO3,-.321300E+02,-.463048E+02,..108412E+02 ,-.647514E-02,..594806E-06 ,
ENTHAL,    HOCL,-.228000E+02,-.482196E+01,..237997E+01 ,-.191517E-03,-.646545E-07,
ENTHAL,     HO2, .500300E+01,-.411792E+01,..211313E+01 ,..123101E-02 ,-.171379E-06,
ENTHAL,    HSO2,-.687E+02    ,..179E+02    ,.0.0         ,.0.0         ,.0.0         ,
ENTHAL,    HSO3,-.416E+02    ,-.713E+02    ,..107E+02    ,-.281E-01    ,..515E-05    ,
ENTHAL,      N,..112965E+03 ,..499709E+01 ,..139479E-01 ,-.347594E-04,..904619E-09 ,
ENTHAL,     NCO,..225E+02     ,-.140E+02    ,..407E+01    ,-.174E-02    ,..115E-07    ,
ENTHAL,      NH,..810000E+02 ,..129091E+02 ,-.121565E+01,..352206E-02 ,-.556300E-06,
ENTHAL,     NH2,..400700E+02 ,..129342E+02 ,-.118508E+01,..671648E-02 ,-.122138E-05,
ENTHAL,     NH3,-.109700E+02,-.207634E+01 ,..719233E+00 ,..789566E-02 ,-.150331E-05,
ENTHAL,      N2,         0.0 ,..919872E+01 ,-.585490E+00,..300734E-02 ,-.591488E-06,
ENTHAL,     N2H,..640E+02     ,..123E+02    ,.0.0         ,.0.0         ,.0.0         ,
ENTHAL,    N2H2,..509001F+02 ,-.132358E+02,..362857E+01 ,..397769E-02 ,-.106278E-05,

ENTHAL,    N2H3,..365E+02     ,..215E+02    ,.0.0         ,.0.0         ,.0.0         ,
ENTHAL,    N2H4,..227900E+02 ,-.396174E+02,..904839E+01 ,..765528E-03 ,-.603169E-06,
ENTHAL,    N2O,..196100E+02 ,-.142978E+02,..420865E+01 ,-.171996E-02,..262810E-07 ,
ENTHAL,    N2O2,..407E+02     ,..190E+02    ,.0.0         ,.0.0         ,.0.0         ,
ENTHAL,    N2O3,..198000E+02 ,-.296303E+02,..819425E+01 ,-.496116E-02,..371846E-06 ,
ENTHAL,    N2O4,..271001E+01 ,-.539296E+02,..131631E+02 ,-.950293E-02,..935437E-06 ,
ENTHAL,    N2O5,..270000E+01 ,-.729334E+02,..177761E+02 ,-.155158E-01,..251510E-05 ,
ENTHAL,      NO,..215403E+02 ,..665964E+01 ,-.392199E-01,..214785E-02 ,-.464634E-06,
ENTHAL,     NO2,..791001E+01 ,-.139207E+02,..405853E+01 ,-.171497E-02,..611416E-08 ,
ENTHAL,     NO3,..170000E+02 ,-.496553E+02,..110452E+02 ,-.107534E-01,..140360E-05 ,
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ENTHAL.      O. .5955408E+07,..754319E+01 ,-.432967E+00,.515051E-03 ,-.749714E-07.
ENTHAL.     OH. .963700E+01,..149699E+02 ,-.154237E+01,.354249E-02 ,-.510573E-06.
ENTHAL.     O2.      0.0     ,.729132E+00 , .108269E+01,.122101E-03 ,-.374675E-07.
ENTHAL.      S.      0.0     ,-.142501E+02,.442048E+01 ,-.139737E-01,.316913E-05 .
ENTHAL.    S.C.      0.0     ,.275552E+01 ,.117405E+00 ,.663617E-02 ,.449961E-07 .
ENTHAL.     SH,.346009E+02 ,.177114E+02 ,-.137644E+01,.453424E-02 ,-.758321E-06.
ENTHAL.     SO,.164800E+01 ,-.297550E+01,.184864E+01 ,-.134415E-02,.141017E-06 .
ENTHAL.    SO2,-.709470E+02,-.154966E+02,.453817E+01 ,-.320046E-02,.329749E-06 .
ENTHAL.    SO3,-.945900E+02,-.345590E+02,.453307E+01 ,-.705317E-02,.799262E-06 .
ENTHAL.     S2,.308400E+02 ,-.193496E+01,.193484E+01 ,-.197984E-02,.297056E-06 .
ENTHAL.    S2O,-.135000E+02,-.131108E+02,.437259E+01 ,-.436175E-02,.581790E-06 .
ENTHAL.     S4,.242000E+02 ,-.286525E+02,.109126E+02 ,-.136562E-01,.211204E-05 .
ENTHAL.    CHO,-.2909E+01  , .979512E+00, .109102E+01, .343380E-02,-.790933E-06.
ENTHAL.   CH2O,-.2770E+02  ,-.112147E+02, .311974E+01, .582149E-02,-.147996E-05.
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